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Abstract

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Both Fe(TFPPBr$_8$)Cl and RuTFPPCl$_8$(CO) catalyze the oxidation of cyclohexene with dioxygen and without added coreductant, with 73 and 296 turnovers, respectively, in 24 hours. Although both porphyrins will catalyze reactions with iodosobenzene, showing selectivity consistent with high-valent metal-oxo formation, overall activity with dioxygen is much higher. In accord with earlier work, cyclohexene oxidation by Fe(TFPPBr$_8$)Cl is consistent with a mechanism involving porphyrin-mediated decomposition of alkyl peroxides, which generates free radicals in solution. RuTFPPCl$_8$(CO) is shown to have a photochemical reaction mechanism involving olefin binding to the excited ruthenium porphyrin, resulting in a dramatic increase in the reaction rate upon irradiation with low energy light. This catalyst represents the first stable, effective metalloporphyrin catalyst for olefin oxidation with dioxygen and light.

THE MECHANISM OF CATALYTIC HYDROCARBON OXIDATION
BY MOLECULAR OXYGEN AND
HALOGENATED RUTHENIUM AND IRON PORPHYRINS

Thesis by

Eva Rachel Birnbaum

In Partial Fulfillment of the Requirements
for the degree of
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1995

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Acknowledgment

Abstract

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Abbreviations Used

mCPBA	m-chloroperoxybenzoic acid
OEP	octaethylporphyrin
SCF	supercritical fluid
SC CO$_2$	supercritical carbon dioxide
TBHP	*tert*-butyl hydroperoxide
TDBPP	tetrakis-(2,6-dibromophenyl)porphyrin
TDCPP	tetrakis-(2,6-dichlorophenyl)porphyrin
TDFPP	tetrakis-(2,6-difluorophenyl)porphyrin
TFPP	tetrakis(pentafluorophenyl)porphyrin
TFPPBr$_8$	β-octabromo-tetrakis(pentafluorophenyl)porphyrin
TFPPCl$_8$	β-octachloro-tetrakis(pentafluorophenyl)porphyrin
TMP	tetramesitylporphyrin
TPP	tetraphenylporphyrin

Chapter 1

Introduction to Catalysis with Metalloporphyrins

Science has "explained" nothing; the more we know the more fantastic
the world becomes and the profounder the surrounding darkness.
-- Aldous Huxley, *Along the Road*, pt. 2 (1925).[1]

The whole of science is nothing more than a refinement of everyday
thinking.
-- Albert Einstein, *Out of My Later Years*, ch. 12 (1950).[2]

Oxidation chemistry is one of many arenas in which chemists are attempting to
devise catalysts that achieve the remarkable efficiency, selectivity, and specificity of
enzymes. Cytochrome P-450, a heme-based enzyme involved in respiration, has long
been a target for the generation of a biomimetic catalyst.[3,4] Found in a wide variety of
tissues, this membrane-bound enzyme catalyzes the oxidation of a wide variety of organic
substrates with reductively activated dioxygen.[4] In particular, the ability of P-450 to
selectively activate the more inert C-H bonds is quite desirable for industrial applications.
Although many catalysts have been investigated, this selectivity has yet to be duplicated
by a synthetic system.

The catalytic cycle of cytochrome P-450 is shown in Figure 1.1. From the resting
state as the ferric porphyrin, two reducing equivalents from NADH are required to fully
activate the enzyme. The first reduces the porphyrin to the ferrous state, enabling it to
bind dioxygen. A second electron reduces the bound oxygen complex, and subsequent
addition of two protons induces heterolytic cleavage of the dioxygen bond and release of
a water molecule to form a high-valent metal-oxo iron porphyrin. The iron oxo

intermediate, which has never been isolated from P-450 due to its high reactivity, is generally believed to be an iron(IV)oxo porphyrin radical cation. Although early steps in the cycle are well documented, assignment of the active species is largely by analogy to Compound I of the enzyme horseradish peroxidase (HRP), which has been definitively characterized as an iron(IV)oxo porphyrin π radical cation.[4,5] The active intermediate can also be directly generated with an O-atom donor such as iodosobenzene or peroxide; this "peroxide shunt" pathway is a convenient test for P-450 monooxygenase-like activity in model complexes.

A general technique in catalyst design is to model the active site of an enzyme, in the hope that one small section of the protein will exhibit the same activity as the whole. The porphyrin core of P-450 lends itself to this type of study for several reasons: reliable syntheses for porphyrins have been developed, the periphery of the porphyrin ligand is easily modified to alter the properties of the porphyrin, and the ligand has distinctive spectroscopy which facilitates investigation. Indeed, the past two decades have produced a plethora of work on metalloporphyrin derivatives.[4,6,7]

Initial investigations on a derivative of the naturally occurring protoporphyrin IX (Figure 1.2) demonstrated that a species spectroscopically similar to compound I could be generated with an O-atom donor.[8] However, rather than oxidizing substrate, this intermediate hydroxylated its own β-side chain. A synthetic analog, octaethylporphyrin, was even less stable outside of the protective protein environment. Although a high-valent iron-oxo was believed to be generated in the presence of iodosobenzene, the planar porphyrin degraded by hydroxylation at the meso position, followed by complete destruction of the porphyrin chromophore. Oxidation of a second porphyrin molecule was clearly more favorable than oxidizing substrate.[8] The protein fold, which protects the porphyrin against autooxidation, prohibits unproductive μ-oxo dimer formation, and enhances substrate-porphyrin interactions, is clearly vital for these simple planar hemes to act as catalysts. A more stable porphyrin molecule would be necessary to mimic

monooxygenase behavior in solution. And so the quest to design a better porphyrin ligand began.

A simple iron tetraphenylporphyrin, Fe(TPP)Cl, was found to oxidize hydrocarbons in the presence of PhIO.[9] Substitution at the meso position with a bulky phenyl moiety was found to reduce aggregation in solution and protect the reactive meso position from reactions leading to porphyrin degradation. Oxidation of tetramesitylporphyrinato-iron(III) chloride (Fe(TMP)Cl) with m-chloroperoxybenzoic acid at low temperatures produced a species that both shares spectral features with Compound I and is capable of epoxidizing alkenes.[10] Although more promising than OEP, these ligands still showed substantial degradation in solution.

The second generation of metalloporphyrin catalysts were designed to increase the lifetime of porphyrins in solution by reducing their susceptibility to oxidative degradation. Halogenation of the meso phenyl rings would raise the reduction potential as well as increase steric bulk along the porphyrin periphery, decreasing the likelihood of dimerization or hydrogen abstraction by other porphyrin molecules. Tetrakis-(pentafluorophenyl)porphyrin (TFPP) was indeed found to be more stable than TPP, and iron complexes were found to show high selectivity for epoxidation of olefins.[11] Similarly, tetrakis(2,6-dichlorophenyl)porphyrinato-iron(III) chloride [Fe(TDCPP)Cl] was found to show high activity with pentafluoroiodosobenzene.[12] Iron(III), manganese(III) and chromium(III) complexes of TDCPP all exhibited higher activity for cyclohexene oxidation with iodosobenzene than their TPP analogs, as well as higher selectivity for epoxide formation. Furthermore, the 2,6-dichlorophenylporphyrin complexes remained intact after an oxidation reaction, while the tetraphenylporphyrin complexes were completely degraded.[13]

In addition to halogenation, other elegant methods have been developed for generating steric barriers against the close approach of two porphyrin molecules. Tailed porphyrins (Figure 1.3) have an imidazole or other nitrogen containing function linked to

the porphyrin ring by a flexible hydrocarbon chain, allowing it to swing around and axially bind to the metal center in simulation of histidine coordination.[14] Picket fence,[15] strapped,[16] basket handle,[17] and capped[18] porphyrins have large organic groups that project perpendicular to the plane of the porphyrin as pickets, or, in the latter cases, actually bridge across from one side of the porphyrin ring to the other. All of the above methods provide some steric protection as well as a pocket in which the substrate may bind. Although these types of porphyrins have led to some extremely interesting work in the area of enantioselective and regioselective oxidation chemistry,[19] they have not been further pursued as general oxidation catalysts. The hydrocarbon side chains that drive the selectivity found with these metalloporphyrins, while stable enough under mild conditions, are susceptible to degradation in a highly oxidizing environment.

Instead of building a pocket around the porphyrin, the third generation catalysts have completely protected the porphyrin periphery by full substitution at both the meso and beta positions (Figure 1.4). Steric bulk from mesityl,[20,21] pentafluorophenyl,[21-28] or 2,6-dihalophenyl[22,29-32] groups at the meso carbons is paired with electron-withdrawing substituents at the β-carbons. The electronic and steric crowding created by the full periphery imparts unusual structural and spectroscopic features to the porphyrin ligand, while the steric bulk of these complexes causes severe distortion of the porphyrin macrocycle, preventing dimerization (Chapter 2 and 3). The electronic demands of the substituents have been shown to decrease oxidative degradation of the porphyrin, thereby increasing net activity.[22,28,29,33,34]

Indeed, these highly halogenated porphyrins are found to be active catalysts. Iron and manganese complexes of β-octachloro, β-octabromo,[20,22,26,28-30,34-40] and β-octanitro[32] tetraphenylporphyrin derivatives are reported to catalyze the oxidation of both alkanes and alkenes with a variety of O-atom donors, with tremendous increases in both activity and catalyst lifetime over the second generation porphyrins. For example, β-octabromo-tetramesitylporphyrinato-manganese(III) chloride catalyzes the epoxidation

of cyclooctene with hydrogen peroxide in 96% yield,[34] and the hydroxylation of adamantane with KHSO$_5$ in 62% yield.[20] Iron(III) chloride complexes of β-octachloro-tetrakis(2,6-dichlorophenyl)porphyrin catalyze the hydroxylation of heptane with iodosobenzene in 80% yield.[22] These reactions show increases in rate, total activity, selectivity, and porphyrin lifetime relative to the unhalogenated derivatives.

An even more unique finding is the activity of the third generation porphyrins with dioxygen. At 80 °C and 75 atm O$_2$, β-octabromo-tetrakis(pentafluorophenyl)-porphyrinato-iron(III) chloride (Fe(TFPPBr$_8$)Cl) catalyzes 17,150 turnovers of isobutane to *tert*-butyl alcohol in three hours. At slightly lower temperatures, the selectivity of the reaction for the desired alcohol can be increased to 92%.[26]

The unprecedented activity of a metalloporphyrin with dioxygen and without a coreductant gave rise to new ideas for mechanisms for O$_2$ activation. Most recent porphyrin literature examines catalysis with O-atom donors that attempt to directly mimic enzymatic P-450 reactions. The reports of Fe(TFPPBr$_8$)Cl activity imply that alternate mechanisms may exist in addition to traditional high-valent metal-oxo chemistry, and prompted a more thorough investigation of this and similar third generation compounds in our lab.

This brief review of recent metalloporphyrin catalysis literature is not meant to be comprehensive, but rather to explain some of the history behind the development of the unusual perhalogenated porphyrin ligand. The more contemporary metalloporphyrin catalysts are now only distant cousins to the natural hemes they were initially designed to model. The following chapters are a more thorough investigation of the spectroscopy and catalytic properties of several fluorinated metalloporphyrins.

Chapter 2 describes the synthesis of halogenated iron and ruthenium porphyrins and their precursors. Molecular structures of β-octachloro-tetrakis(pentafluorophenyl)-porphyrinato-ruthenium(II) carbonyl, [RuTFPPCl$_8$(CO)] and the zinc and free ligand precursor complexes, are shown to be extremely distorted, in line with other halogenated

porphyrin structures. ^{19}F NMR is developed as a method for characterizing the solution structure of both paramagnetic and diamagnetic fluorinated porphyrin structures.

The unusual spectroscopy and electrochemistry of halogenated porphyrins is discussed in Chapter 3. The changes in the frontier orbital energies upon phenyl and pyrrole halogenation are described. A full molecular orbital diagram is shown for RuTFPPCl$_8$(CO) and discussed in terms of the distortion and electron-withdrawing effects of halogenation.

Enhanced catalytic activity is observed with the highly halogenated complexes. Alkene oxidation by halogenated iron porphyrins is described in Chapter 4. Fe(TFPPBr$_8$)Cl is an active catalyst with both iodosobenzene and dioxygen, and shows a significant increase in activity and catalyst lifetime relative to Fe(TFPP)Cl. Observations support a mechanism involving porphyrin-mediated decomposition of alkyl peroxide, as proposed earlier in our group.[37,41]

Chapter 5 is a discussion of catalysis with RuTFPPCl$_8$(CO). Similar to the iron complex, this porphyrin is an extremely active catalyst for the oxidation of olefins under very mild conditions: 1 atm dioxygen, room temperature, and without addition of co-reductant. Alkene oxidation is also observed with iodosobenzene. Observations of oxidation reactions catalyzed by RuTFPPCl$_8$(CO) with dioxygen are not consistent with mechanisms proposed for the activity of either the iron analog, Fe(TFPPBr$_8$)Cl, or other ruthenium porphyrins. Instead, olefin oxidation is dependent on light, possibly initiated by an interaction of the alkene with a RuTFPPCl$_8$(CO) excited state. As oxidation mechanisms in metalloporphyrins involving electronic excited states are rare, a photochemical reaction mechanism would be an interesting result, suggesting intermediates and ideas completely distinct from traditional high-valent metal-oxo chemistry.

The final chapter investigates the use of halogenated porphyrin catalysts in supercritical carbon dioxide. An apparatus was set up to measure the solubility of three

halogenated porphyrins in supercritical carbon dioxide by optical spectroscopy. Each porphyrin was tested with both iodosobenzene and dioxygen as a catalyst for the oxidation of cyclohexene in a supercritical medium. Although the results are extremely preliminary, they suggest that selectivity was more affected than net activity by the change in solvent. More multiple oxidations of the same substrate molecule were observed relative to reactions run in methylene chloride. Supercritical carbon dioxide was shown for the first time to be a good medium for oxidation catalysis.

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Figure 1.1 -- The proposed catalytic cycle for oxidation reactions by cytochrome P-450.
All steps before the generation of the high-valent metal-oxo are well
documented, but the actual active intermediate has not been isolated.
Addition of an O-atom donor such as iodosobenzene to the ferric porphyrin
(peroxide shunt) will directly form the oxidizing species, generally believed to
be $Fe^{IV}(P)(O)^{\cdot+}$ (diagram modified from reference 1).
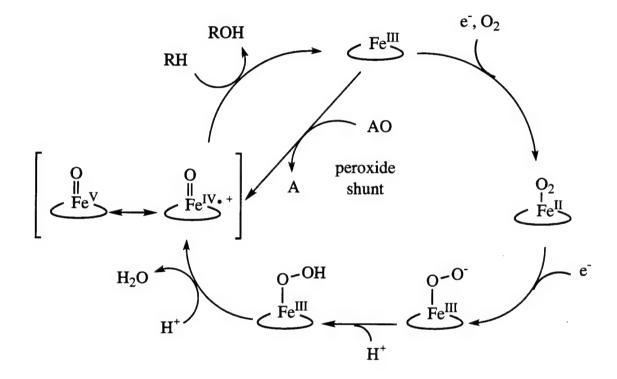
Figure 1.2 -- Diagram of the heme center from cytochrome P-450, protoporphyrin IX, and a synthetic equivalent, octaethylporphyrin (OEP). Naturally occurring hemes commonly bear alkyl or vinyl substituents at the pyrrole carbons.

Protoporphyrin IX (above) and Octaethylporphyrin (OEP)

Figure 1.3 -- Representations of tailed, picket fence, basket handle, and capped porphyrins. The bulky ligands create a steric barrier in the plane perpendicular to the porphyrin to prevent μ-oxo dimerization.

= porphyrin ring
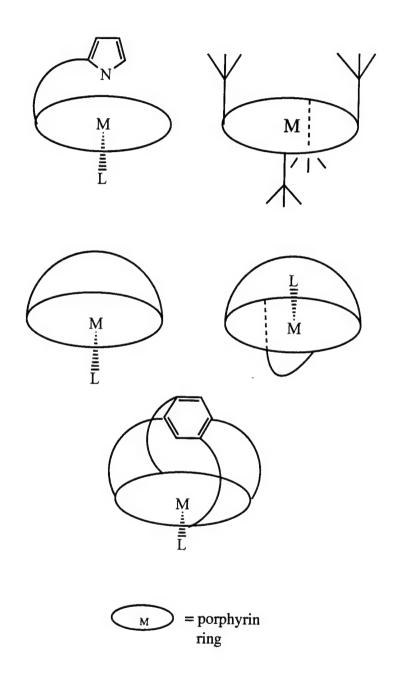
Figure 1.4 -- Drawings of three iron complexes of second generation porphyrins showing
the groups commonly substituted at the meso positions: mesityl,
2,6-dichlorophenyl, and pentafluorophenyl groups. Halogenation of the
pyrrole carbons would form third generation catalysts.

Fe(TMP)Cl

Fe(TDCPP)Cl

Fe(TFPP)Cl

Chapter 2

Synthesis, Molecular Structures, and
Nuclear Magnetic Resonance Spectroscopy
of Halogenated Porphyrins

Introduction

Biomimetic metalloporphyrin oxidation catalysts are often based on a
tetraphenylporphyrin template because these complexes are not as susceptible to
aggregation and are protected from degradation to oxophlorins (oxo substitution at the
meso position) by meso-phenyl substitution. Mesityl (TMP) or 2,6-dichlorophenyl
(TDCPP) groups at the meso positions are more successful than unsubstituted phenyl
rings, since the additional steric bulk of a substituted phenyl moiety decreases the tendency
to form μ-oxo dimers in solution. The next generation of metalloporphyrins further
enhanced the tetraphenylporphyrin ligands with electron-withdrawing substituents at the
beta positions, removing reactive C-H bonds from the porphyrin periphery and increasing
the steric bulk of the molecules. Many β-substituted TDCPP and TMP metalloporphyrins
have been synthesized and investigated as oxidation catalysts (see Chapter 4). In addition
to these ligands, another option is to begin with a tetrakis(pentafluorophenyl)porphyrin
(TFPP) template, and then halogenate the β-positions to give a perhalogenated macrocycle.
These "Teflon" porphyrins are designed to be extremely resistant to normal porphyrin
decomposition in oxidizing environments.

Although extremely efficient porphyrin condensation reactions have been
developed,[1] allowing porphyrins to be made in high yield from the appropriate
benzaldehyde and pyrrole, this methodology has not been reported to be successful for
β-halo derivatives. Recent advances have developed a the synthesis for the required

3,4-halogenated pyrroles,[2,3] but these compounds readily polymerize and are difficult to purify. Instead, halogenation of the β-positions is accomplished on an intact porphyrin macrocycle.[4-14] The fluorinated porphyrin, 5,10,15,20-tetrakis(pentafluorophenyl)-porphyrinato-zinc(II) (ZnTFPP), is commercially available or can be synthesized from pyrrole and pentafluorobenzaldehyde. The zinc, rather than the unmetallated porphyrin, is used because the metallated porphyrins are found to better withstand the halogenation reactions.[14]

Synthesis

Halogenation to form β-octachloro- or β-octabromo-tetrakis(pentafluorophenyl)-porphyrinato-zinc(II) (ZnTFPPCl$_8$ and ZnTFPPBr$_8$; Figure 1.1) was initially accomplished with direct addition of $Cl_{2(g)}$ or $Br_{2(l)}$. However, a less hazardous synthesis with N-halo-succinamide was developed[10] and found to proceed in good yield. Addition of excess N-halosuccinamide to a refluxing solution of ZnTFPP in methanol gave the desired product in 1-3 hours. Synthesis of the octabromo porphyrin was easier to drive to completion than that of the octachloro. The relative size of chlorine (atomic radii = 0.99) versus bromine $(1.14 \text{ Å})^{15}$ would have predicted a more difficult synthesis for ZnTFPPBr$_8$ based on the greater steric demands of eight bromines on the porphyrin periphery . However, the relative ease of synthesis of the two ligands suggests that the electronic effect, which leads to a decrease in reactivity for further substitution on the ligand, (electronegativity = 3.617 Cl, 3.365 Br)[16] is more significant. If the trend follows to fluorine, the lack of success in our lab[14] in synthesizing the β-octafluoro porphyrin is not surprising.

Although ZnTFPPBr$_8$ was readily purified by column chromatography, the large amount of partially halogenated porphyrins in the ZnTFPPCl$_8$ reaction mixture necessitated high performance liquid chromatography (HPLC). Once the β-octahalo porphyrins were isolated, they were demetallated with $HCl_{(g)}$ and purified from the zinc salts by alumina

chromatography. The yields for $H_2TFPPCl_8$ and $H_2TFPPBr_8$ were 40 and 82%, respectively, based on ZnTFPP.

Iron was inserted into the porphyrins by the standard methods: iron(II) acetate in refluxing glacial acetic acid or iron(II) chloride in DMF.[17,18] With the TFPPBr$_8$ ligand, the metal is oxidized to iron(III) during the aqueous workup, and the porphyrin isolated as the chloride salt, Fe(TFPPBr$_8$)Cl. The iron porphyrins were found to demetallate during standard column chromatography, and could only be purified by washing or recrystallization. Therefore, high quality free ligand was a prerequisite for generation of pure iron porphyrin.

Addition of pyridine to a solution of Fe(TFPPBr$_8$)Cl reduced the metal and formed the bis-pyridine adduct. Both Fe^{III}(TFPPBr$_8$)Cl[19] and Fe^{II}(TFPPBr$_8$)py$_2$[20] have been crystallographically characterized. The absorption spectrum of [Fe(TFPPCl$_8$)] in the presence of pyridine indicates formation of Fe(TFPPCl$_8$)py$_2$, but this species was not isolated. Attempts to synthesize [Fe(TFPPCl$_8$)] were made using air-free, high vacuum techniques, in hopes of isolating a clean, oxygen-free sample for the anticipated investigation of O_2 activation. In retrospect, the removal of oxygen is believed to have complicated its synthesis. Allowing oxygen into the synthesis of Fe(TFPPBr$_8$)Cl did not lead to oxygen coordination, but clean oxidation of the Fe^{II} porphyrins to Fe^{III}(TFPPBr$_8$)Cl. In the absence of oxygen, the β-octachloro porphyrin appeared to form an iron(II) complex, based on the red shifted Soret band (see Chapter 3), but with mixed axial ligands. Due to the difficulty in isolating any pure Fe(TFPPCl$_8$) species, further work concentrated on the β-octabromo species.

Insertion of Ru from Ru$_3$(CO)$_{12}$ into H_2TFPPX_8 in perfluorobenzene yields a bright red (X = Cl) or green (X = Br) RuTFPPX$_8$(CO) compound.[21] In perprotiobenzene, the extended time at reflux necessary to insert the ruthenium atom results in partial porphyrin dehalogenation and decomposition. In these reactions, ruthenium also inserts into the partially chlorinated derivatives $H_2TFPPCl_7$ and $H_2TFPPCl_6$ to form

$RuTFPPCl_7(CO)$ and $RuTFPPCl_6(CO)$, which can be isolated by sequential column chromatography and HPLC (Figure 2.2).

A single band attributable to CO stretching (1990, Cl_8; 1973 cm^{-1}, Br_8) is observed in the IR spectrum of $RuTFPPX_8(CO)$, confirming a single carbonyl ligand.[22] Identification of the other axial ligand is problematic; this ligand is labile in $Ru(CO)$ porphyrins due to the strong trans effect of the CO.[23] Photolysis of $RuTFPPCl_8(CO)$ in pyridine results in the formation of $RuTFPPCl_8(py)_2$. After photolysis, a single symmetrically coordinated species is observed by ^{19}F NMR spectroscopy, indicating that the multiple signals in the spectrum of the carbonyl complex are due to variations in trans ligation and not dehalogenation of the porphyrin ring (*vide infra*).

Ruthenium insertion from $Ru_3(CO)_{12}$ was found to proceed in very low yield: approximately 10-20 % for $TFPPCl_8$, and less than 5 % for $TFPPBr_8$. Attempts to modify the reaction were unsuccessful. Solvent choice is limited, since any proton bearing solvent will exchange protons with the β-halogens of the porphyrin. Other ruthenium starting materials were tried, including $Ru(DMSO)_4Cl_2$, $[Ru(DMSO)_6]Cl_2$, $RuCl_3$, and $[Ru_5Cl_{12}]^{2-}$ (generated in situ). None showed significant reactivity with the $TFPPCl_8$ ligand.

Surprisingly, attempts to insert ruthenium into TFPP were also unsuccessful. Similar reaction conditions as above showed no reaction with H_2TFPP before substantial decomposition of the ligand occurred. No reports of RuTFPP have been found in the literature, although many metallated derivatives of TFPP have been synthesized.

Molecular Structures

ORTEP diagrams for $H_2TFPPCl_8$, $ZnTFPPCl_8$,[10] and $RuTFPPCl_8(CO)H_2O$[24] complexes are shown in Figure 2.3 - 2.5, with the atom numbering shown. Complete crystallographic reports are included in Appendix 2.

$H_2TFPPCl_8$ crystallized from an acetone/water solution in space group $P\bar{1}$, with two porphyrins in the unit cell. The two parallel porphyrin molecules are 4.74 Å apart, with the porphyrin centers slightly offset (center to center distance 6.1 Å). The zinc derivative, $ZnTFPPCl_8$, crystallized from a saturated o-dichlorobenzene solution with a solvent molecule in a parallel plane both above and below the porphyrin molecule. The solvent molecules are located 3.4 Å from the mean plane of the porphyrin (defined as the average plane of the four nitrogen atoms), a distance suggestive of a π-stacking interaction between the π systems of the porphyrin and the o-dichlorobenzene molecules. Aromatic solvent molecules were found to stack in a similar fashion in the crystal structure of tetraphenylporphyrinato-zinc(II) bis-toluene, $ZnTPP(C_6H_5CH_3)_2$, where two toluene molecules occupy these positions.[25] The π donor ability of the aromatic solvent may help stabilize the zinc ion in the electron deficient macrocycle. Similarly, $H_2TFPPBr_8$ was found to crystallize with an o-dichlorobenzene molecule stacked above each porphyrin molecule.[10]

Recrystallization of $RuTFPPCl_8(CO)$ in air from ethyl acetate and hexane gave $RuTFPPCl_8(CO)H_2O$ (Figure 2.5). An ethyl acetate molecule is hydrogen bonded to the water ligand (O ⋯ O 2.668 Å), and the stability provided by this hydrogen bond network may explain why no crystals were obtained with other solvents. Trans coordination of CO and H_2O to Ru is unusual, but is precedented in $RuOEP(CO)H_2O$ and the non-porphyrin compound $trans$-$RuCl_2(PEt_3)_2(CO)H_2O$.[26,27]

Chlorination of the β-pyrrole carbons induces severe tetrahedral distortions (Figures 2.6 and 2.7) reducing the molecular symmetry of the porphyrin from D_{4h} to D_2. The pairs of β-halogen atoms are located alternately above and below the average plane determined by the four central nitrogen atoms, and the phenyl rings are rotated slightly towards the mean porphyrin plane to minimize steric contact between the halogen atoms at the pyrrole positions and the ortho carbons of the pentafluorophenyl rings. The distortion of the macrocycle is quantified as the distances of the $meso$ and β-carbons from the mean

plane of the porphyrin (Table 2.2). A view of the free ligand porphyrins H_2TFPP, $H_2TFPPCl_8$, and $H_2TFPPBr_8$ (Figure 2.6), generated from crystal structure coordinates, shows the increasing distortion along the series.

The three β-octachloro porphyrins described above exhibit severe distortions common to perhalogenated and other highly substituted porphyrins:[7,10,13,20,28-32] 'ruffling' or twist (distortion manifested at the *meso-* carbons) and 'saddling' (distortion manifested at the β-carbons).[33] As expected, saddling increases with halogenation (Figure 2.6), as manifested by increasing average C_β displacements from the plane from 0.051 to 0.62 to 0.90 Å in the free ligand series.[10] The free ligand, $H_2TFPPCl_8$, is the least distorted of the structurally characterized chlorinated porphyrins [$ZnTFPPCl_8$, $H_2TFPPCl_8$, $RuTFPPCl_8(CO)H_2O$, $CuTFPPCl_8$[29]], as reflected by the smaller perpendicular displacements of atoms from the mean porphyrin plane and a lack of the twisting or ruffling observed in the metallated derivatives. The saddle distortion in the free ligand (average C_β displacement = 0.62 Å) is smaller than in the metallated derivatives $ZnTFPPCl_8$ (0.75), and $CuTFPPCl_8$ (0.70),[29] but greater than in the octahedrally coordinated $RuTFPPCl_8(CO)H_2O$ (0.48 Å).[24]

Though saddled, the unmetallated $H_2TFPPCl_8$ has essentially no twist distortion (average C_m displacement = 0.023 Å). When the metal atom sits inside the core, a large twist distortion is observed: $ZnTFPPCl_8$ (0.13), $RuTFPPCl_8(CO)H_2O$ (0.20),[24] and $CuTFPPBr_8$ (0.16 Å).[28] Extended to the porphyrin periphery, this results in one halogen atom of each pyrrole being significantly farther out of the mean plane than the other. In $ZnTFPPCl_8$ the displacements differ by 0.31 Å,[10] and in $RuTFPPCl_8(CO)H_2O$ by 0.43 Å.[24] The twist distortion is apparent in the side-on view of $RuTFPPCl_8(CO)H_2O$ (Figure 2.7).

A final measure of distortion is one based on the phenyl dihedral angles; to minimize steric contact with the β-substituents, the phenyl rings rotate towards the mean porphyrin plane (Figure 2.6). The dihedral angles decrease with halogenation from 79° in

H_2TFPP to 73° in $H_2TFPPCl_8$ to 54° in $H_2TFPPBr_8$. Metallation also affects the dihedral angle. In the $TFPPCl_8$ complexes, octahedral $RuTFPPCl_8(CO)$ has a much larger dihedral angle (81°) than the free ligand (73°) or the zinc complex (59°) (Table 2.3).

Remarkably, bond lengths (Table 2.4) in the porphyrin skeleton are essentially preserved throughout the series of metalloderivatives of TPP,[25,34,35] TFPP, and $TFPPX_8$ (X= Cl, Br).[10,36] Bond lengths and angles in the porphyrin skeleton are very similar for all three $TFPPCl_8$ species, indicating that metallation does not greatly affect porphyrin bond lengths.

The Ru-C bond is slightly longer in $RuTFPPCl_8(CO)H_2O$ (Table 2.2) than in $RuOEP(CO)H_2O$ (1.785)[26] or $RuTPP(CO)EtOH$ (1.77 Å),[37] consistent with the relatively high value of v_{CO}.[22] The Ru-C-O bond is nearly linear in the three porphyrins, at 178.9, 178.5, and 175.8°, respectively. The Ru-O bond length (2.172 Å) is shorter for the perhalogenated porphyrin than for $RuOEP(CO)H_2O$ (2.253 Å), and closer to the distance found for *trans*-$RuCl_2(PEt_3)_2(CO)H_2O$ (2.189 Å).[26,27] Interestingly, although the Ru-N bond lengths in $RuTFPPCl_8(CO)H_2O$ and $RuTPP(CO)EtOH$ are the same (~2.05 Å), the TPP derivative is planar, whereas the metal in the halogenated derivative is 0.11 Å out of the mean plane towards the carbonyl ligand. The distorted structure decreases the core size, and may explain why ruthenium insertion is so difficult for $TFPPCl_8$ and has almost no yield for $TFPPBr_8$.

NMR Spectra

Fluorine-19 NMR has been extremely helpful in ascertaining both the identity and purity of halogenated compounds. The 100% natural abundance of spin 1/2 ^{19}F and its high gyromagnetic ratio allow ^{19}F NMR spectra to be obtained readily.[38] As observed in ^1H NMR of tetraphenylporphyrins, the corresponding fluorine atoms from all four phenyl rings appear equivalent in ^{19}F NMR. The four phenyl rings on the porphyrin are related in the high degree of symmetry of the approximate D_{4h} or D_{2d} point groups of these

compounds. The chemical shifts of the fluorine atoms on the meso-phenyl rings are extremely sensitive to the metal center, its axial ligands, and the pyrrole carbon substituents, however, such that each porphyrin has a unique spectrum. Correlations in ^{19}F shifts and splitting patterns may be related to various TFPP structures.

The ^{19}F NMR for the unmetallated and zinc TFPP and TFPPCl$_8$ complexes (Figure 2.8; Table 2.5) display one set of signals each for the ortho, meta, and para fluorines. The para signal, identified by its intensity of 1/2 relative to the ortho and meta signals, is most sensitive to metallation, and shifts 1.7 ppm upfield from H$_2$TFPPCl$_8$ to ZnTFPPCl$_8$. The signal appears as a triplet due to coupling to the meta-Fs ($^3J_{F-F}$ = -21 Hz). The ortho signal, farthest downfield, is split into a doublet of doublets, and the meta is a triplet of doublets. The additional splitting is attributed to coupling of fluorines positioned para to one another, as only the para signal does not show any additional structure, with $^5J_{F-F}$ = 6.7 Hz. Computer simulation of the observed spectrum with only these parameters was not satisfactory. Additional coupling between meta fluorines of $^4J \approx$ -2 Hz was needed to increase linewidth and generate the proper intensities in the model spectrum. The signs of the coupling constants are consistent with literature values, as are the magnitudes of the various Js (ortho > para > meta).[39]

Substitution with a paramagnetic or an axially unsymmetric metal center results in significantly different NMR spectra. As with proton NMR, fluorine resonances of the paramagnetic species exhibit a large isotropic shift from those of the diamagnetic derivatives. High spin five-coordinate Fe[III]TFPP(Cl) (Figure 2.9) or Fe[III]TFPP(OH) samples, identified by their characteristic UV-Vis and EPR spectra,[40] show *five* separate ^{19}F NMR signals that fall over a much larger window than those of the diamagnetic porphyrins. The ortho and ortho' (and meta and meta') fluorines, no longer related by an S$_4$ axis, now have chemical shifts separated by several ppm, and previously observed fine structure is lost due to paramagnetic line broadening. The resonances do not coalesce at temperatures up to 298 K, indicating that rotation of the phenyl rings is slow on the NMR

time scale at room temperature. A Curie plot (Figure 2.10) shows a linear relationship between the isotropic shift and inverse temperature. The isotropic shift is the sum of a contact shift (dependent on 1/T) and a dipolar shift (dependent on $1/T^2$)[41]; the linear dependence on 1/T suggests that the dipolar contribution is small. However, the lines do not intersect the origin, which may indicate some dipolar contribution is present.[42]

The axial ligand is known to affect the ^{1}H NMR shifts of paramagnetic Fe^{III} porphyrins. In general terms, the porphyrin and the axial ligand compete for bonding interactions with the metal, and the strength of these interactions affects the ring current and π electron density on the protons and therefore their chemical shift.[43] A substantial downfield shift of all five resonances (Table 5) is observed upon substitution of an $^-$OH for a Cl$^-$ ligand on FeTFPP, consistent with axial ligand effects observed with p-CH$_3$-TPPMnX complexes. Increased π bonding between the metal and the stronger field axial ligand reduces π electron density in the porphyrin, resulting in smaller contact shifts in the ^{1}H NMR spectrum.[44] Although the direction of the shift is similar in the fluorine spectrum, the different magnitudes for the contact shift at the ortho and para positions relative to the meta are not observed. Therefore, contact shift alone is not sufficient to explain the ^{19}F NMR spectrum. This is consistent with theory that expects a large temperature independent paramagnetic contribution to fluorine chemical shifts (relative to proton). Further study involving additional compounds would be needed to fully explore this effect.

The five-coordinate (FeTFPP)$_2$O dimer also shows 5 peaks in its NMR spectrum (Figure 2.11); however, the signals show significantly less broadening and appear in a much narrower window than the other Fe^{III} porphyrins. Strong antiferromagnetic coupling between the two metal centers[40] reduces the paramagnetic shift in the ^{19}F NMR of the μ-oxo dimer. Similarly, the resonance for the β-hydrogens in the ^{1}H NMR spectrum is shifted less in the dimer relative to the monomeric iron(III) complexes. The pyrrole protons of (FeTFPP)$_2$O and (FeTPP)$_2$O[42] show similar isotropic shifts of 5.1 and 5.02 ppm,

respectively, from the diamagnetic Zn complexes, whereas the pyrrole protons are shifted over 70 ppm downfield in the spectrum of Fe(TFPP)Cl.

The distinctive patterns observed in ^{19}F NMR play important roles in the structural assignment of other perhalogenated compounds. The ^{19}F NMR spectrum of $Fe^{III}TFPPBr_8(Cl)$ (Figure 2.12) shows a broadened five-signal pattern similar to that of $Fe^{III}TFPP(Cl)$. The ortho fluorine resonances exhibit a smaller paramagnetic shift in the perhalogenated compound, consistent with the mixed spin character of the $Fe^{III}TFPPBr_8(Cl)$ ground state.[20] The addition of pyridine to $Fe^{III}TFPPBr_8(Cl)$ results in reduction of the iron and formation of the symmetric bis-pyridine compound, $Fe^{II}TFPPBr_8(py)_2$. The assignment of this compound was confirmed as low-spin iron(II) due to the sharp signals and splitting pattern consistent with an axially symmetric, diamagnetic species. Most unusual is the NMR of $[Fe^{II}TFPPBr_8(Cl)]^-$, produced by electrochemical reduction of $Fe^{III}TFPPBr_8(Cl)$ (Figure 2.13a). The relatively sharp signals support the reduction of the metal center, but the splitting of the ortho and meta signals suggests an axially unsymmetric porphyrin; the Fe(II) porphyrin appears to retain an association with the chloride ligand even in the reduced state.[19] Chemical reduction in methanol with ascorbic acid, however, gives a very different spectrum. Only three resonances appear instead of five, indicating a symmetric porphyrin, most likely the bis-methanol derivative $[Fe^{II}TFPPBr_8(OMe)_2]$.

NMR also revealed interesting properties of $RuTFPPCl_8(CO)H_2O$.[24] Although an X-ray structure for this compound was obtained, ^{19}F NMR on crystalline material fails to yield a simple spectrum. Instead, several 5-signal patterns are observed, suggesting that the strong trans effect of the carbonyl ligand results in lability of the sixth ligand. The unsymmetric trans coordination around the Ru again leads to dual ortho and meta signals (as in FeTFPP(Cl)), but with the diamagnetic metal center, the fine structure is retained. Upon photolysis in pyridine, a single species, $RuTFPPCl_8(py)_2$, is obtained. The simple pattern now seen in the ^{19}F NMR shows that previous overlapping signals were due to

multiple species with varying ligands trans to the CO rather than to partial decomposition or dehalogenation of the porphyrin macrocycle.

Conclusions

A series of tetrakis(pentafluorophenyl)- and β-octahalo-tetrakis(pentafluorophenyl)-porphyrins have been synthesized. TFPP derivatives have been studied to provide a comparison for understanding the spectroscopy and catalytic properties of the perhalogenated iron and ruthenium complexes (Chapters 3 - 6).

Crystal structures of unmetallated, zinc, and ruthenium octachloro-tetrakis(pentafluorophenyl) porphyrins are consistent with other structures that demonstrate that halogenation of the β-pyrrole carbons causes a severe saddling of the porphyrin macrocycle. The free base porphyrin, however, does not show the twisting distortion seen in the metallated octahalo derivatives, suggesting that the metal plays a significant role in determining the type and degree of distortion.

The distortions and metal effects observed in the structures of the halogenated metalloporphyrins are analogous to those reported for the octamethyl and octaethyl derivatives of TPP; 2,3,7,8,12,13,17,18-β-octaalkyl-5,10,15,20-tetraphenylporphyrin (TPPX$_8$, X = methyl, and ethyl).[32,45] ZnTPPMe$_8$ and ZnTPPEt$_8$ are essentially the steric analogs of ZnTFPPCl$_8$ and ZnTFPPBr$_8$, respectively. The implication is that the observed distortion is a result of the steric interactions involving the β-halo substituents, and is not electronic in origin.

Fluorine-19 NMR has been shown to be a useful tool for characterization of perhalogenated porphyrin compounds. The identification of various FeTFPPX species will allow another mechanism to study catalysis reactions, for example, by monitoring deactivation of the catalyst via formation of a μ-oxo dimer. Trends in linewidths, shift dispersions, and multiplicities all provide information on the oxidation state and coordination sphere of the metal center. As a supplement to crystallographic data, NMR

allows a more direct examination of the behavior of these highly halogenated porphyrins in solution.

Experimental

Materials Omnisolv grade methanol, acetone, dichloromethane, benzene, pyridine, dimethylformamide, and hexane were purchased from EM Science. N-chloro- and N-bromosuccinimide, glacial acetic acid, iron(II) chloride, triruthenium dodecacarbonyl, and tetraphenylporphyrinato ruthenium(II) carbonyl were purchased from Aldrich and used as received. ZnTFPP and H$_2$TFPP were purchased from Porphyrin Products and used as received. UV-Vis (CH$_2$Cl$_2$): ZnTFPP λ_{max} nm (ε 10^5 M^{-1} cm^{-1}); 414 (5.0), 544 (0.24); H$_2$TFPP λ_{max} nm 412, 506, 584. Fe^{III}TFPPCl was purchased from Aldrich and purified by chromotography on alumina before use. UV-Vis (acetone): λ_{max} nm (ε 10^5 M^{-1} cm^{-1}) 350 (0.7), 410 (1.0), 50 (0.11), 629 (0.06). RuTPP(py)$_2$ was prepared by a literature method.[46]

Methods UV-Vis spectra were recorded on a Hewlett Packard HP8452 diode array interfaced to an IBM or a Cary-14 spectrophotometer with an Olis 3820 conversion system. Infrared spectra were recorded as solutions in carbon tetrachloride or benzene on a Perkin-Elmer Model 1600 FT-IR spectrophotometer. Separation of the ruthenium porphyrins was accomplished with a Beckman Model 126 dual pump and 166 single channel detector on a Vydac C-18 reverse phase column. A 1000 W tungsten lamp was used for photolysis experiments. ^{1}H and ^{19}F NMR spectra were recorded on a Brüker AM-500 (tuned down to 470.56 MHz for fluorine detection) instrument in CDCl$_3$ or deuterated acetone and referenced internally to C$_6$H$_5$F at -113.6 ppm (vs. CFCl$_3$ at 0 ppm). Porphyrin purification was accomplished with alumina (Fluka or Baker 40 μ alumina) or silica (Analtech 150 Å pore, 75-100 particle size silica) column chromatography. Further purification of the zinc and ruthenium perhalogenated porphyrins was accomplished with a Beckman Model HPLC system (126 dual pump and 166 single channel detector) on a

Vydac C-18 reverse phase column with isocratic acetone:water elution. Mass spectroscopy was performed at Caltech with a cesium ion fast atom bombardment spectrometer. Elemental analysis on the perhalogenated compounds was obtained, and varied greatly by compound. Results were not satisfactory, even on crystalline samples that were pure by other criteria.

$Fe^{III}TFPP(OH)$ and $(Fe^{III}TFPP)_2O$: $Fe^{III}TFPP(OH)$ and $(Fe^{III}TFPP)_2O$ were synthesized from the chloride by published methods:[40] $Fe^{III}TFPP(Cl)$ was dissolved in benzene, and a small amount of NaOH solution was added. After stirring for several hours, the water was removed using a separatory funnel, and the benzene solution was chromatographed on neutral alumina with a benzene/acetone solution. The μ-oxo elutes first, and the hydroxide elutes with a higher percent acetone. $Fe^{III}TFPPP(OH)$: UV-Vis (acetone): λ_{max} 406, 563 nm. $(Fe^{III}TFPP)_2O$: UV-Vis; CH_2Cl_2; λ_{max} 398, 415(shoulder), 560 nm.

$H_2TFPPCl_8$: Chlorination of ZnTFPP was accomplished by a modification of earlier methods.[8,47,48] Approximately 500 mg ZnTFPP was dissolved in 50 mL dry methanol with forty equivalents of N-chlorosuccinimide, and the mixture refluxed for an hour. When chlorination of the pyrrole positions was complete, as determined by the red shift of the Soret band in the UV-Vis and thin layer chromatography on silica plates (1:1 hexane: dichloromethane) the solution was allowed to cool. The product was precipitated with water, filtered, and washed with cold hexane to remove decomposed porphyrin by-products. Further purification by HPLC was necessary to separate partially chlorinated species. Yield $ZnTFPPCl_8$ 60 to 80%. UV-Vis (CH_2Cl_2): λ_{max} nm (ε 10^5 M^{-1} cm^{-1}); 364, 440 (1.6), 572 (0.13). Mass spectrum m/z = 1314 (calc. 1313). The chlorinated zinc porphyrin was demetallated as previously by Lyons, et al.:[47] $ZnTFPPCl_8$ was redissolved in approximately 50 mL chloroform, and HCl gas was passed through a gas dispersion tube into the solution for 1-2 minutes. The volume of the reaction mixture was reduced, and the solution was chromatographed on alumina, eluting with 95% chloroform - 5%

methanol. The product, $H_2TFPPCl_8$, was collected and rotary evaporated to dryness, with a yield of approximately 95%. UV-Vis (CH_2Cl_2): λ_{max} nm (ε 10^5 M^{-1} cm^{-1}); 436 (16), 536 (1.3), 622 (0.46).

$H_2TFPPBr_8$: The bromo analog was similarly synthesized via bromination of ZnTFPP with N-bromosuccinimide. $ZnTFPPBr_8$: UV-Vis (CH_2Cl_2): λ_{max} nm (ε 10^5 M^{-1} cm^{-1}); 460 (1.9), 594 (0.17). The free ligand was obtained by demetallation with HCl gas, and the product chromatographed on alumina. UV-Vis (CH_2Cl_2): λ_{max} 454, 552, 636 nm.

FeTFPPBr$_8$(Cl) and [FeTFPPCl$_8$]: Iron was inserted into H_2TFPPX_8 with freshly prepared iron(II) acetate in glacial acetic acid,[17] or with $Fe^{II}Cl_2$ in DMF.[18] Insertion was evident by the red color of the solution. The iron porphyrin was precipitated with brine, dried, and washed with hexane to remove impurities. UV-Vis (CH_2Cl_2) Br_8: λ_{max} nm(ε 10^5 M^{-1} cm^{-1}) 402 (8.1), 442 (8.5), 560 (1.4). With $H_2TFPPCl_8$, reactions were conducted on a high vacuum line and precipitated with deoxygenated water. UV-Vis (CH_2Cl_2): λ_{max} 404, 582 nm. Addition of pyridine to a solution of FeTFPPX$_8$(Cl) led to formation of $Fe^{II}TFPPX_8(py)_2$. UV-Vis (CH_2Cl_2) Br_8: λ_{max} 450, 556, 588 nm; Cl: λ_{max} 438, 542, 574 nm.

RuTFPPCl$_8$(CO): The preparation of RuTFPPCl$_8$(CO) was based on the methods of Tsutsui[49] and Chow.[50] 300 mg $H_2TFPPCl_8$[10] reacts with 300 mg $Ru_3(CO)_{12}$ (48 h, refluxing benzene) to form RuTFPPCl$_8$(CO). RuTFPPCl$_7$(CO) and RuTFPPCl$_6$(CO) also were isolated from the reaction mixture. RuTFPPCl$_n$(CO) (n = 6,7,8) complexes were separated from unreacted free ligand by column chromatography on silica gel eluting with hexane and increasing percentages of methylene chloride. The partially chlorinated isomers were purified by HPLC, and the identity of each fraction was confirmed by mass spectroscopy. The parent peak in each mass spectrum appears at the mass for RuTFPPCl$_n$ (n = 6,7,8), with a smaller peak appearing at the mass for the monocarbonyl complex. Parent peaks appeared at m/z = 1351.2 (RuTFPPCl$_8$) , 1315.8

(RuTFPPCl$_7$), and 1280.1 (RuTFPPCl$_6$). UV-Vis (CH$_2$Cl$_2$): λ_{max} nm (ε 10^5 M^{-1} cm^{-1}) 416 (1.7), 542 (0.14). RuTFPPBr$_8$(CO) (mass spectrum; m/z =1703) was synthesized from Ru$_3$(CO)$_{12}$ and H$_2$TFPPBr$_8$ (50 h refluxing benzene). UV-Vis (CH$_2$Cl$_2$): λ_{max} 424, 560 nm.

RuTFPPCl$_8$(py)$_2$: Photolysis of the carbonyl was accomplished by modification of Chow's methods.[50] Pyridine solutions of RuTFPPCl$_n$(CO) exposed to a 1000W mercury lamp for several hours lose a carbonyl ligand to form RuTFPPCl$_n$(py)$_2$. Loss of the carbonyl was confirmed by the disappearance of the CO stretch (IR, CCl$_4$ solution) and by ^{19}F-NMR spectroscopy (CDCl$_3$ solution): d (RuTFPPCl$_8$(py)$_2$) = -138.7 (2F, q, ortho); -152.3 (1F, t, para); -163.2 ppm (2F, m, meta). UV-Vis (CH$_2$Cl$_2$): λ_{max} 415, 510, 536 nm. ^{19}F-NMR: -138.7 (2F, q, ortho), -152.3 (1F, t, para), -163.2 ppm (2F, m, meta).

Crystal Structure Analysis: Since the halogenated porphyrin crystals lost solvent easily, a single crystal was removed directly from the crystallization solution and mounted in a capillary with silicon grease. Data were collected on an Enraf-Nonius CAD-4 diffractometer using Mo Ka radiation. Atomic scattering factors and values for f' were taken from Cromer and Waber[51] and Cromer,[52] and CRYM,[53] MULTAN,[54] and ORTEP[55] computer programs were used for calculations. The weights were taken as 1/σ^2(F$_o$^{2}); variances (σ^2(F$_o$^{2})) were derived from counting statistics plus an additional term, (0.014I)^2; variances of the merged data were obtained by propagation of error plus another additional term, (0.014 $\bar{I}$)^2.

Purple crystals of ZnTFPPCl$_8$ were grown from a saturated solution of *o*-dichlorobenzene at 0 ˚C. Crystals of this compound lost solvent quickly, so one was covered with epoxy glue before being cooled to -44 ˚C on the diffractometer. The zinc crystal was found to be tetragonal, belonging to space group P$\bar{4}$2$_1$c. The structure was solved by location of the zinc atom from a Patterson map. Structure factors and Fourier calculations showed Cl1 and Cl2, and subsequent structure factor Fourier calculations gave the rest of the porphyrin. Solvent molecules were found in difference Fourier maps

calculated in their planes. The solvent molecules occupy two separate regions in the cell, each region holding one dichlorobenzene molecule. The molecules are disordered in these regions, and were initially modeled with idealized $C_6H_4Cl_2$ groups. Eventually, some of the chlorine atoms of the solvent were refined, as well as the population parameters for alternate orientations, but the carbon atoms were always positioned based on Fourier maps. For one region (C31-36 and C41-46) anisotropic displacement parameters were assigned by hand based on the maps and the refined parameters of the Cl atoms of the solvent; the other carbon atoms of the solvent were left isotropic. The disordered solvent regions are the cause, in all probability, of the somewhat larger than usual values for R and goodness of fit.

Brown crystals of $H_2TFPPCl_8$ were grown by slow evaporation from an acetone/water solution. The crystals were found to be triclinic, belonging to space group $P\bar{1}$. Porphyrin molecules were located from a Patterson map, and the two inner hydrogen atoms were located in a difference map as disordered among the four nitrogen atoms. Their positional parameters were refined, with B values fixed at 1.2 times the isotropic equivalent U_{ij} value of the bonded nitrogen atoms and the population factors assigned at one-half.

Deep red crystals of $RuTFPPCl_8(CO)(H_2O)$ were grown by slow evaporation from an ethyl acetate/hexane solution. Ruthenium atom coordinates were obtained from a Patterson map, and the remaining atoms located with structure factor-Fourier calculations. Hydrogen atoms on the solvent molecules were positioned by calculation in idealized locations with staggered geometry and a C-H bond length of 0.95 Å. Of the solvent molecules, only one ethyl acetate site is fully populated (C71,C72, O2, O3, C73, and C74). The second (C81, C82, O4, O5, C83, and C84) is half-populated, near a center of symmetry. The region occupied by hexane is not easily interpreted. There are five peaks in a difference map in an area of broadly diffuse electron density. These five were co-planar within 0.15 Å, so we fitted idealized hexane molecules to the difference density in this plane. Our model has three orientations of the hexane; there may be twice that many. We

kept the positional and thermal parameters of these idealized molecules fixed but refined their population parameters independently. The sum of the three was 0.84; we believe this represents some loss of hexane from the crystal during data collection. We kept the populations fixed in the final refinement. The final difference map has peaks of 0.88, 0.82 and 0.79 Å^{-3} and valleys of -1.24 and -0.84 Å^{-3} in this region.

Appendix 2 contains unit cell diagrams, final heavy atom parameters, anisotropic displacement parameters, complete distances and angles, and structure factors for $H_2TFPPCl_8$, $ZnTFPPCl_8$, and $RuTFPPCl_8(CO)H_2O$, H atom parameters for $H_2TFPPCl_8$, and intermolecular distances less than 3.5 Å for $ZnTFPPCl_8$ and $RuTFPPCl_8(CO)H_2O$.

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Figure 2.1 -- The general structure of third generation pentafluorophenyl metalloporphyrins discussed in this chapter. The α, β, and meso carbons are marked.

$M = H_2$, Zn, Fe, Ru
$X = H$, Cl, Br
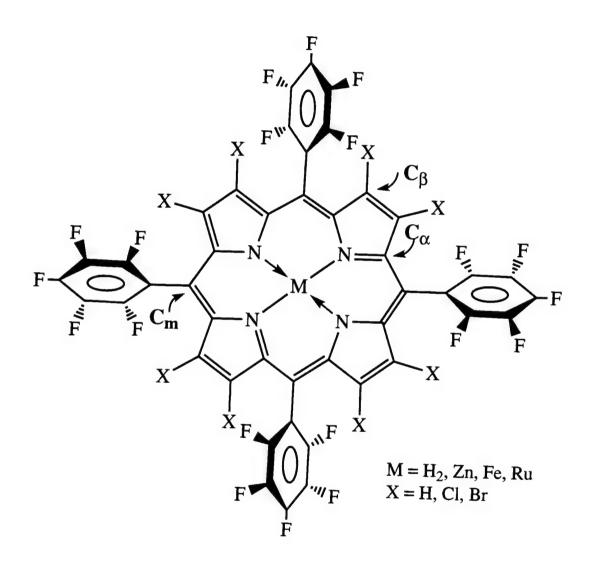
Figure 2.2 -- HPLC trace showing separation of partially halogenated ruthenium

porphyrins on a reverse phase C_{18} column with isocratic elution of 88%

ethanol in water. Excess free ligand comes off the column earliest, followed

by ruthenium porphyrins bearing increasing numbers of β-chlorines. Zinc

porphyrin is likely produced from metallation of the free ligand in the

stainless steel HPLC tubing.
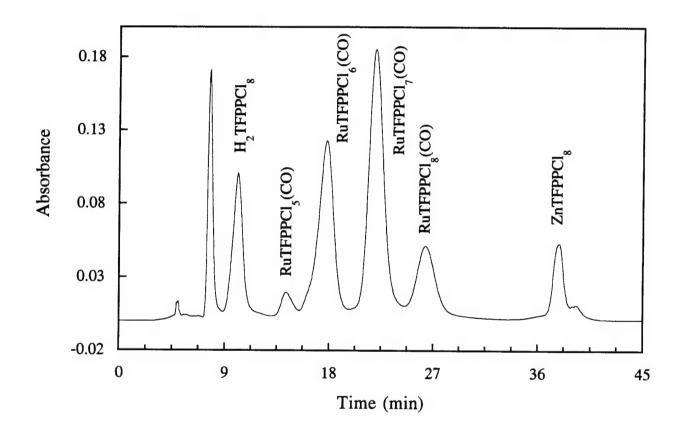
Figure 2.3 -- ORTEP diagram of $H_2TFPPCl_8$ with 50% probability ellipsoids of the
molecule showing the numbering used. Only two hydrogen atom sites are
shown.
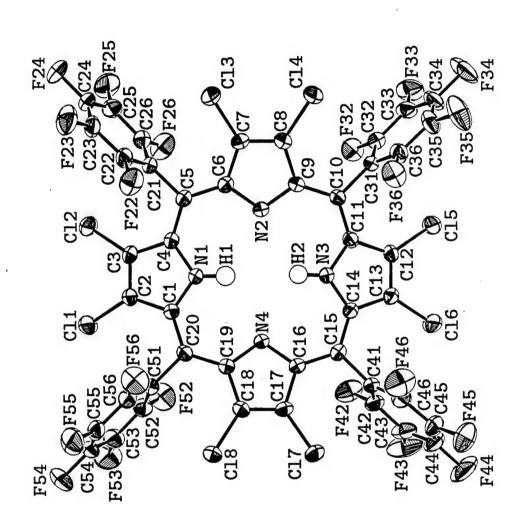
Figure 2.4 -- ORTEP diagram of ZnTFPPCl$_8$ with 50% probability ellipsoids of the molecule showing the numbering system used.
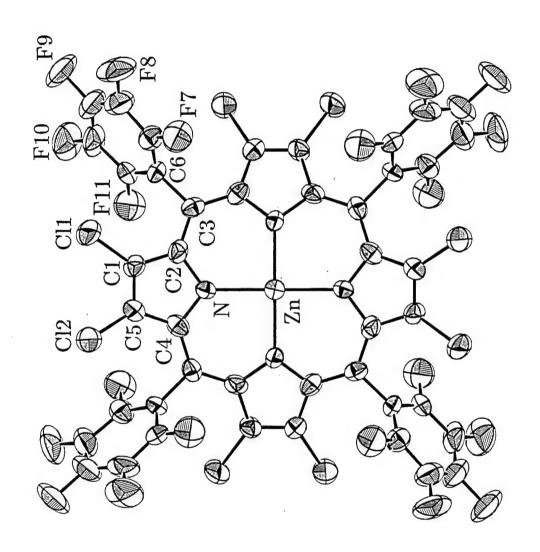
Figure 2.5 -- ORTEP diagram of $RuTFPPCl_8(CO)H_2O$ with 50% probability ellipsoids showing the numbering system used. Atoms C21, C31, C41, and C51 (not numbered) are bonded to C3, C8, C13, and C18, respectively; carbon atoms in the pentafluorophenyl groups have the same numbers as the attached fluorine atoms.
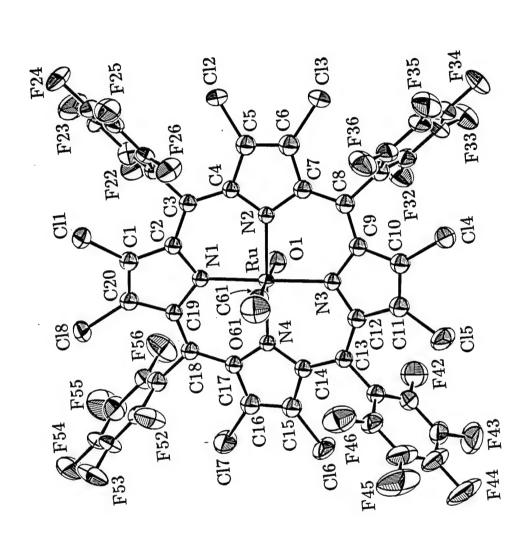
Figure 2.6 -- Molecular representations of the series H_2TFPP, $H_2TFPPCl_8$, and
$H_2TFPPBr_8$ using the actual crystal structure coordinates. From the planar
H_2TFPP, the saddle distortion clearly increases upon further halogenation.
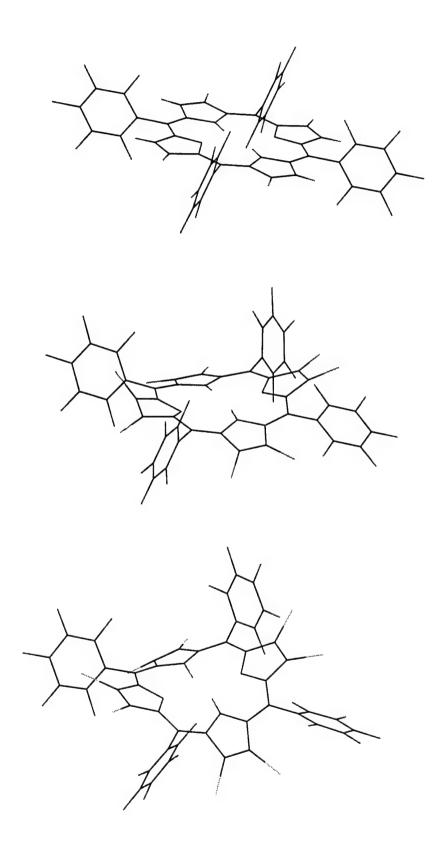
Figure 2.7 -- Edge-on view of a Chem 3D drawing of RuTFPPCl$_8$(CO)H$_2$O using crystal structure coordinates. The ruffle in the porphyrin macrocycle is apparent in the different displacements of the chlorine atoms (striped) from the mean porphyrin plane.
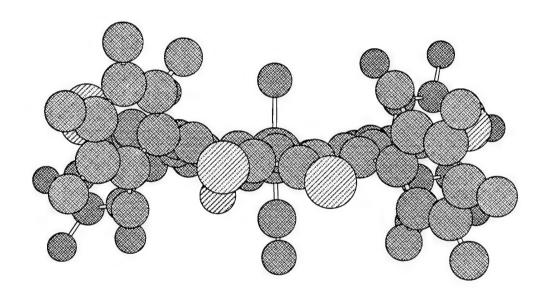
Figure 2.8 -- ^{19}F-NMR spectra of a) $H_2TFPPCl_8$ and b) $ZnTFPPCl_8$ in $CDCl_3$. The
signals are assigned ortho, para, meta, from left to right. The signals for the
free ligand have been enlarged to show the fine structure observed in the
spectra of free ligand, zinc, and other diamagnetic metal porphyrins.
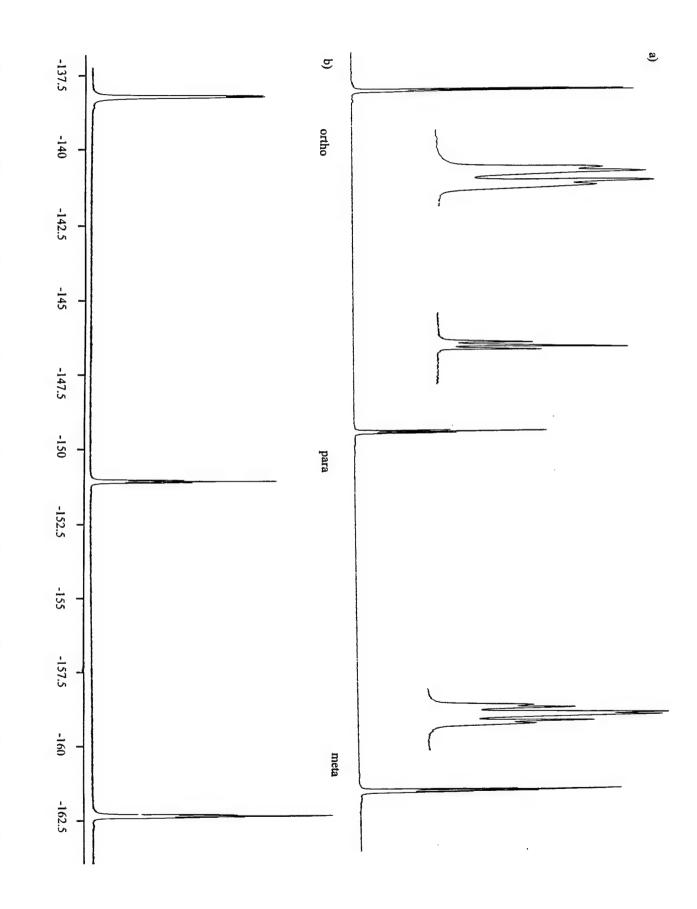
Figure 2.9 -- ^{19}F-NMR spectrum of Fe^{III}TFPP(Cl). The ortho resonances are shifted over 20 ppm downfield from those of H$_2$TFPP.
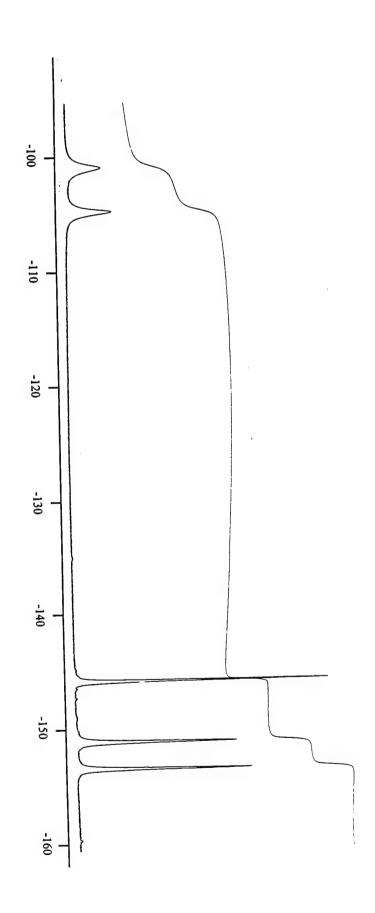
Figure 2.10 -- Curie plot showing the temperature dependence of the chemical shift of Fe^{III}TFPP(Cl) resonances. The isotropic shift is calculated relative to the diamagnetic Zn^{II}TFPP complex.
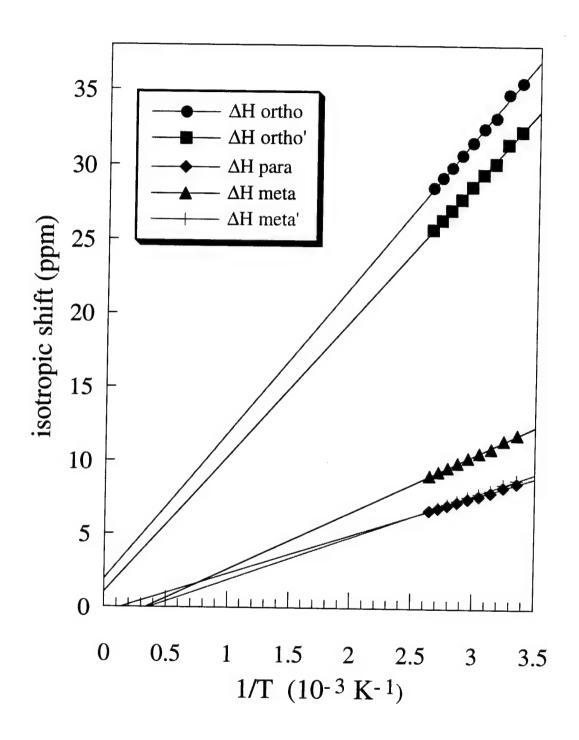
Figure 2.11 -- ^{19}F-NMR spectrum of $(Fe^{III}TFPP)_2O$ in acetone-d_6. The window is much

smaller than that of the paramagnetic FeTFPP(Cl) monomer due to

antiferromagnetic coupling between the two iron atoms.

PPM
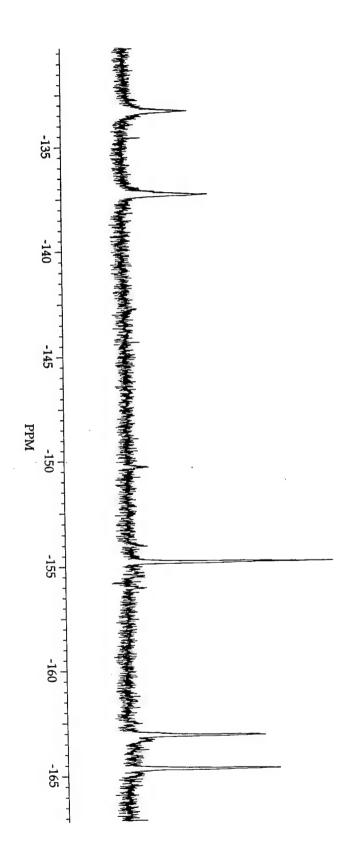
Figure 2.12 -- ^{19}F-NMR spectrum of $Fe^{III}TFPPBr_8Cl$ in acetone-d_6. The paramagnetic

shift is less than in the partially halogenated FeTFPP(Cl).

PPM
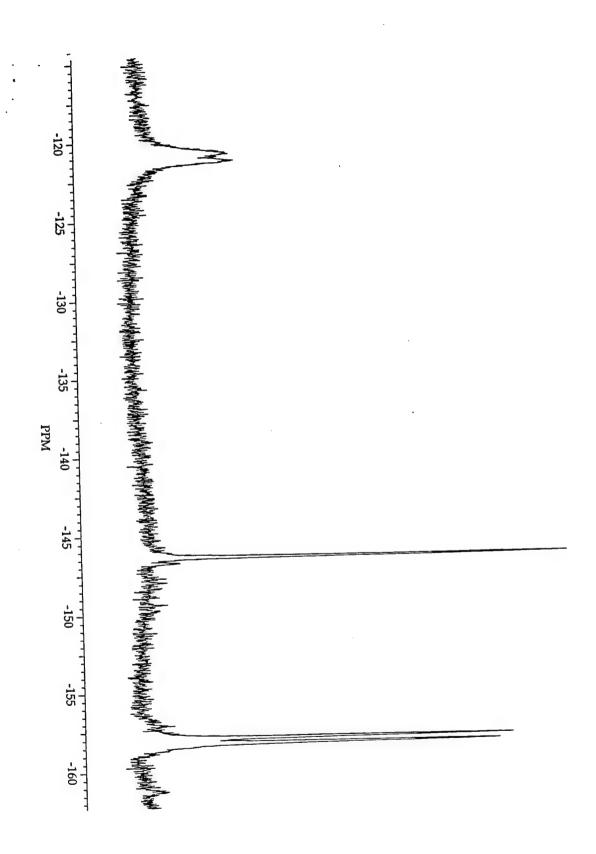
Figure 2.13 -- ^{19}F-NMR spectra of electrochemically (bottom) and chemically (top) generated [Fe^{II}TFPPBr$_8$]. The five line pattern in the electrochemically generated spectrum indicates an axially unsymmetric species, [Fe^{II}(TFPPBr$_8$)Cl]$^-$, while the lack of splitting in the ortho and meta resonances in the top spectrum is suggestive of a symmetric coordination sphere, i.e. Fe^{II}(TFPPBr$_8$)(OMe)$_2$. The five spikes in the bottom spectrum are instrument noise.
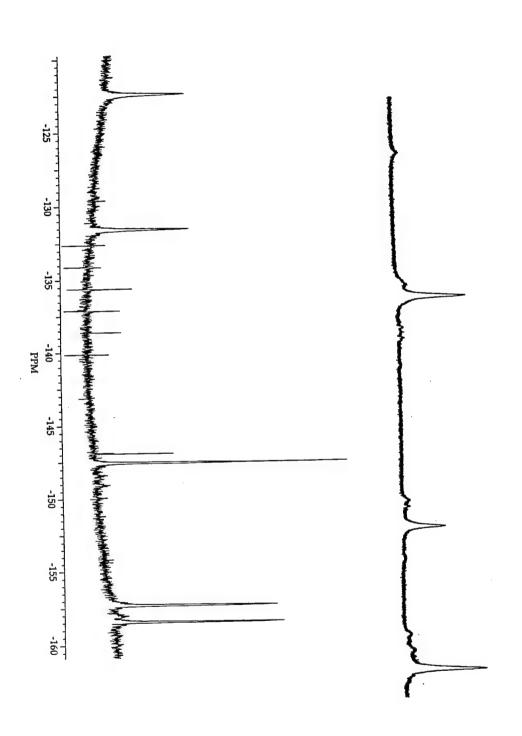
Table 2.1. X-ray Experimental Parameters.

	$H_2TFPPCl_8$	$ZnTFPPCl_8$	$RuTFPPCl_8(CO)H_2O$
formula	$C_{44}H_2Cl_8F_{20}N_4$	$C_{44}Cl_8F_{20}N_4Zn$ $\cdot 6(C_6H_4Cl_2)$	$C_{57}H_{28}Cl_8F_{20}N_4O_5$ Ru
molecular weight	1250.12	2139.48	1613.53
color	brown	dull red	dark red
shape	plate	thick needles	rectangular tablet
crystal system	triclinic	tetragonal	monoclinic
space group	$P\bar{1}$	$P\bar{4}2_1c$	$P2_1/c$
a, Å	11.066(1)	19.502(20)	14.364(3)
b, Å	14.641(3)		16.012(4)
c, Å	14.678(2)	10.916(8)	26.679(8)
a, °	88.97(1)		
β, °	76.05(1)		90.29(2)
γ, °	71.29(1)		
V, Å^3	2181.4(6)	4152(6)	6136(3)
Z	2	2	4
D_x, g cm^{-3}	1.90	1.71	1.75
radiation	MoKα		
μ, cm^{-1}	6.4	10.41	7.11
temperature, K	293	229	295
crystal size, mm	0.11 X 0.35 X 0.42	0.19 X 0.19 X 0.59	0.16 x 0.29 x 0.44
diffractometer	Enraf-Nonius Cad-4		
collection method	omega scans		
$h_{min/max}$	± 12	0/23	-15/+15
$k_{min/max}$	± 16	0/23	-17/+17
$l_{min/max}$	± 16	± 13	0/28
reflections measured	12455	8027	16,813
indep. reflections	6054	2050	8006
reflections used	6054	2050	8005
$R_{int}(F)$	0.019	0.033	0.043
R(F)	0.042	0.0949	0.089
$R_w(F^2)$	0.0061	0.0286	0.028
$(\Delta/\sigma)_{max}$	0.01	0.07	0.00 (for porphyrin)
goodness of fit	2.05	3.29	2.14

Table 2.2. Selected Average Bond Lengths (Å).

Bond	$H_2TFPPCl_8$	$ZnTFPPCl_8$	$RuTFPPCl_8(CO)H_2O$
$N - C_\alpha$	1.372	1.380	1.378
$C_\alpha - C_\beta$	1.448	1.427	1.448
$C_\beta - C_\beta$	1.347	1.337	1.339
$C_\alpha - C_m$	1.402	1.403	1.399
N - M (or H)	0.94	2.032	2.059
N - Ct	2.075	2.029	not determined
Ru - C	—	—	1.828
Ru - O	—	—	2.172

Table 2.3. Selected Average Angles (°).

Angle	$H_2TFPPCl_8$	$ZnTFPPCl_8$	$RuTFPPCl_8(CO)H_2O$
N - M - N	—	90.2	175.5
$C_\alpha - N - C_\alpha$	109.5	106.9	177.6
$N - C_\alpha - C_m$	125.4	124.2	125.1
$N - C_\alpha - C_\beta$	107.2	107.4	107.8
$C_\alpha - C_\beta - C_\beta$	107.9	108.8	108.0
$C_\alpha - C_m - C_\alpha$	125.8	126.5	126.0
$C_m - C_\alpha - C_\beta$	127.2	128.4	127.0
Dihedral (C_6F_5 groups)	72.6	59.1	80.7
C - Ru - O	—	—	177.6

Table 2.4. Average Deviations of Atoms from the Least-Squares Plane (Å).

Atom	$H_2TFPPCl_8$	$ZnTFPPCl_8$	$RuTFPPCl_8(CO)H_2O$
N	0.088	0.10	0.06
C_m	0.023	0.13	0.20
C_β	0.625	0.79, 0.68	0.48
Cl_{odd}	1.06	1.17	1.11
Cl_{even}	1.06	1.48	0.68
M	—	0.0	0.11 (towards CO)

Table 2.5: NMR Shifts for Halogenated Porphyrins.

Compound	NMR values in acetone-d_6[a]				
	^{19}F			^{1}H	β-H
	ortho	para	meta	N-H	
ZnTFPP	-138.5 (d)	-154.8 (t)	-163.7 (m)	—	9.17
H$_2$TFPP	-136.9 (d)	-151.7 (t)	-161.8 (m)	-2.91	9.40
FeTFPP(Cl)	-105.8, -107.7	-150.2	-153.9, -156.0	—	83
FeTFPP(OH)	-108.0, -114.5	-152.0	-156.6, -158.0	—	83
(FeTFPP)$_2$O	-133.3, -137.1	-154.8	-163.1, -164.7	—	14.3
ZnTFPPCl$_8$	-138.9 (d)	-151.5 (t)	-163.4 (m)	—	—
H$_2$TFPPCl$_8$	-140.0 (d)	-149.8 (t)	-162.4 (m)	-1.0[b]	—
RuTFPPCl$_8$(CO)[c]	-138.8, -139.3	-151.3 (t)	-163.2, -163.6	—	—
RuTFPPCl$_8$(py)$_2$	-136.9 (d)	-149.7 (t)	-161.1 (m)	—	—
ZnTFPPBr$_8$	-138.4 (d)	-151.7 (t)	-163.4 (m)	—	—
H$_2$TFPPBr$_8$	-139.7 (d)	-150.1 (t)	-162.7 (m)	-0.5[b]	—
FeTFPPBr$_8$(Cl)	-121.4, -122.3	-146.5	-158.1, -158.5	—	—
[FeTFPPBr$_8$(Cl)]$^-$ [d]	-124, -133	-148	-158, -160	—	—
[FeTFPPBr$_8$][e]	-136	-152	-163	—	—
FeTFPPBr$_8$(py)$_2$[f]	-138.6	-152.0	-163.1	—	

a. ^{19}F-NMR values are versus CFCl$_3$ at 0 ppm. ^{1}H-NMR values are versus TMS at 0 ppm. Fine structure given as follows: (d) doublet of doublets, (t) triplet, (m) multiplet.

b. Very broad; the inner nitrogen protons are much more distinct in chlorocarbon solvents such as CDCl$_3$.

c. Major set of resonances, each with fine structure as observed in diamagnetic species; other resonances are also observed, as discussed in text.

d. Produced by bulk electrolysis.

e. Produced by reduction with ascorbic acid in methanol. Presumably the bis-methanol complex (see text).

f. Values in CDCl$_3$.

Spectroscopy and Electronic Structures of
Halogenated Porphyrins

Introduction

Metalloporphyrins have distinctive UV-visible spectroscopy due to the aromatic porphyrin chromophore. Two strong $\pi \rightarrow \pi^*$ absorptions in the near UV ($\log \varepsilon \approx 5$ M^{-1} cm^{-1}) and visible regions ($\log \varepsilon \approx 4$ M^{-1} cm^{-1}) dominate the spectrum. The higher energy transition is known as the Soret (or B) band, and the less intense, lower energy transition as the Q band. Other higher energy bands of moderate intensity often appear, designated N, L, and M with increasing energy. A typical porphyrin spectrum is pictured in Figure 3.1, with the various transitions labeled with standard porphyrin nomenclature.[1]

A satisfactory theoretical basis for these bands was developed by extension of work on polyarenes,[2,3] which developed a new method for calculating frontier molecular orbital energies for extended π systems. LCAO calculations were based on a postulate assuming free electron movement along the perimeter of the π system. Essentially, this allowed the porphyrin macrocycle to be treated as an 18-electron polyarene; after several iterations, the now-standard Gouterman four orbital model for porphyrin spectroscopy evolved from these calculations.[4,5] The frontier orbital picture is as follows (Figure 3.2); in D_{4h} symmetry, the two lowest occupied molecular orbitals consist of a nearly degenerate a_{1u} and a_{2u} pair, and the highest unoccupied molecular orbitals are a degenerate e_g set, both of π symmetry. Generally, the a_{1u} orbital is found at slightly lower energy than the a_{2u}, resulting in the two observed electronic transitions. Strong configurational interactions between the lowest energy states give rise to the different intensities in the Soret and Q bands.[5]

Although $\pi \rightarrow \pi^*$ in origin, the two intense transitions observed in porphyrin spectra are remarkably sensitive to the metal coordination sphere and oxidation state. In

combination with NMR data, UV-visible spectroscopy is a valuable tool for porphyrin characterization, and in some situations, is the sole method of characterization for some intermediates in metalloporphyrin oxidation reactions.

The substituents on the porphyrin periphery are found to effect the relative energies of the porphyrin frontier molecular orbitals. Substitution at the β-positions of the porphyrin ring with electron withdrawing groups such as halogens or cyano groups has been found to substantially red-shift the Soret band.[6-8] A combination of theoretical and experimental work has separated the effects of halogenation into electronic[9-13] and steric[14-17] factors. Electrochemical data and semi-empirical calculations have both suggested that electron withdrawing substituents on the porphyrin periphery stabilize both the HOMO and the LUMO. This effect is offset by the distortion of the porphyrin macrocycle, which results in a large destabilization of the HOMO, and a smaller destabilization of the LUMO (Figure 3.2). The different magnitude of these shifts results in a red shifted electronic transition.[14,15,18,19] Characterization of non-planar β-alkyl porphyrins supports this separation of electronic and steric effects.[15] Similar to β-halo-porphyrins, these complexes have red-shifted Soret bands from the distortion-induced destabilization of frontier orbitals; however, the reduction potentials for these compounds are substantially more negative than in halogenated derivatives.

Results and Discussion

The electronic spectroscopy of the perhalogenated porphyrins described in Chapter 2 is consistent with this electronic model. The UV-Vis spectra for the zinc(II) tetraphenylporphyrin series are in Figure 3.3. Fluorination of the phenyl moiety has little effect on the Soret or Q band positions, consistent with the planar structures for both these compounds.[20,21] In fact, rather than the red shift observed with pyrrole halogenation, a slight blue shift in the Soret band is observed for both the zinc and free base porphyrins. The direction of the change may be explained by the effect of meso substitution on the

relative energy of the porphyrin HOMOs. The a_{2u} orbital, which has greater electron density at meso position,[5] is stabilized by the pentafluorophenyl groups such that it falls at lower energy than the a_{1u} orbital.[22] The a_{1u} orbital, with no density at the meso position, remains relatively unchanged in energy, resulting in a larger HOMO-LUMO gap for the TFPP compounds. Electrochemical experiments also show that the HOMO shifts more than the LUMO, as ZnTFPP is 0.57 V more difficult to oxidize, but only 0.38 V harder to reduce than ZnTPP.

The effect of pyrrole substitution is more substantial. Chlorination induces a 1405 cm^{-1} red shift in the Soret energy of ZnTFPPCl$_8$ relative to ZnTFPP; as expected, the larger bromine atom induces a greater shift (2405 cm^{-1}) in ZnTFPPBr$_8$. The magnitude of the shift is consistent with other halogenated porphyrins, i.e., H$_2$TMP exhibits a 2210 cm^{-1} red shift upon bromination.[23] The decrease in Soret intensity is offset by increasing strength of the Q bands (Table 3.1), consistent with a decrease in the configurational interaction upon β-halogenation.[18] However, the oscillator strength throughout the zinc porphyrin series remains fairly constant: 2.58, 3.40, 2.5, and 2.8 M^{-1} cm^{-2} (from ZnTPP to ZnTFPPBr$_8$).[24]

The anodic shift in the reduction potentials of ZnTFPPX$_8$[25] and H$_2$TFPPX$_8$ relative to the TFPP complexes (Table 3.2) also indicate that electron-withdrawing groups at the β positions stabilize both the highest occupied and lowest unoccupied molecular orbitals of tetraphenylporphyrins. Furthermore, the reduction potentials reflect the contraction of the HOMO-LUMO gap observed in the spectroscopy. Relative to H$_2$TFPP, H$_2$TFPPCl$_8$ is 0.46 V easier to reduce, but only 0.13 V harder to oxidize.

Addition of a redox active metal does not alter the observed trends. The Soret transition red shifts 1808 cm^{-1} from Fe^{III}(TFPP)Cl to Fe^{III}(TFPPBr$_8$)Cl (Figure 3.4), and the Soret bands of the bis-pyridine derivatives, Fe^{II}(TFPPBr$_8$)py$_2$ and Fe^{II}(TFPPCl$_8$)py$_2$, are also found at lower energy than those of Fe^{II}(TFPP)py$_2$ (Table 3.3). Although Fe^{III}(TFPPBr$_8$)Cl may appear to have a split Soret at 404 and 440 nm, the higher energy

absorbance may be a chloride to iron charge transfer, as is the 351 nm band in the spectrum of $Fe^{III}(TFPP)Cl$. As the LMCT falls at closer energy to the Soret, it steals intensity from it, resulting in the unusually large extinction coefficient for this absorption. The reduction potential of the metal ($Fe^{III/II}$) follows the same trend as the ligand upon halogenation, increasing from -0.29, to -0.08, to 0.31 V vs. AgCl/Ag along the series Fe(TPP)Cl, Fe(TFPP)Cl, and Fe(TFPPBr$_8$)Cl.[26]

Electrochemical reduction of Fe(TFPPBr$_8$)Cl is found to red shift the Soret from 440 nm to 478 nm, similar to the 25 nm shift observed in the reduction of Fe(TPP)Cl. Chemical reduction with ascorbic acid in methanol results in a similar but less shifted spectrum (Figure 3.5). NMR (Chapter 2) of both species suggests that the first is a five-coordinate anion, [Fe^{II}(TFPPBr$_8$)Cl]$^-$, and the second a low spin six-coordinate species, likely Fe^{II}(TFPPBr$_8$)(OMe)$_2$. The spectrum obtained during the attempted synthesis of Fe(TFPPCl$_8$) was also at very low energy, 440 nm, suggesting that an Fe^{II} species was transiently formed. Addition of pyridine resulted in an optical spectrum very similar to that of Fe(TFPPBr$_8$)py$_2$, but no single species was isolated.

Following the same trends, the RuTFPPX$_8$(CO) complexes are harder to oxidize and easier to reduce than RuTPP(CO).[27] Notably, the RuTFPPX$_8$(CO)$^{+/0}$ potentials are within 0.07 V of those of the unmetallated H$_2$TFPPX$_8$ molecules, indicating that the first electron is removed from a ligand-based orbital. Oxidation of RuTFPPCl$_8$(py)$_2$ occurs 0.63 V lower than RuTFPPCl$_8$(CO), suggesting that the HOMO is a dπ level in the pyridine derivative. The magnitude of this shift is similar to the 0.64 V shift between the metal-centered oxidation of RuTPP(py)$_2$[28] and the ligand-centered oxidation of RuTPP(CO).[29]

This sterically induced contraction of the HOMO-LUMO gap is surprisingly small for RuTFPPCl$_8$(CO) (0.11 V relative to RuTPP(CO))[27] as extracted from the values of the +/0 and 0/- potentials). Enhanced backbonding from Ru^{II} to TFPPCl$_8$ is the likely explanation of this finding, as discussed below.

The electronic properties of perhalogenated Ru^{II} porphyrins can be interpreted in terms of a Gouterman four-orbital model[4,9] modified by the inclusion of the Ru $d\pi$ orbitals (Figure 3.6).[30] Increased backbonding in the $TFPPX_8$ complexes promotes mixing of $\pi \rightarrow e\pi^*$ and $Ru^{II} \rightarrow e\pi^*$ excited states, with the result that the Soret (mainly $\pi \rightarrow e\pi^*$) transition falls at higher energies than would be predicted by a simple one-electron (HOMO-LUMO) model.[1,31,32] The Soret band of $RuTFPPCl_8(CO)$ (418 nm) is substantially blue-shifted from that of $H_2TFPPCl_8$ (440 nm). A blue shift upon metalation with a 2nd or 3rd row metal is often observed; i.e., the Soret band of $PdTFPPCl_8$ is 705 cm^{-1} shifted from the free ligand. The magnitude of the shift in $RuTFPPCl_8(CO)$, ~ 1300 cm^{-1}, is surprisingly high, indicating that the electronic coupling of Ru^{II} to the porphyrin is unusually strong. The offsetting effect of extensive backbonding in the distorted porphyrins is the reason that the Soret bands for both $RuTFPPCl_8(CO)$ and $RuTFPPCl_8(py)_2$ (414 nm) are only slightly red-shifted from those of $RuTPP(CO)$ (412 nm) and $RuTPP(py)_2$ (413 nm) (Figure 3.7 and 3.8).

IR data also indicate that halogenated porphyrins are π acceptors. The peak attributable to the CO stretch appears at much higher energy in the halogenated porphyrins relative to the 1945 cm^{-1} band observed for $RuTPP(CO)$.[33] The transition energy decreases according to $RuTFPPCl_8(CO)$ (1990) > $RuTFPPCl_7(CO)$ (1987) > $RuTFPPCl_6(CO)$ (1984) > $RuTFPPBr_8(CO)$ (1973 cm^{-1}), further reflecting the increased competition between the porphyrin and the carbonyl ligand for π electron density upon halogenation.

The distortion-induced contraction of the HOMO-LUMO gap[9,10,12,14,17,18] is evidenced by a decrease of the Soret transition energy according to $RuTFPPCl_6(CO)$ (410) > $RuTFPPCl_7(CO)$ (413.5) > $RuTFPPCl_8(CO)$ (418 nm) (Figure 3.9). The Soret band of $RuTFPPBr_8(CO)$ is further red-shifted to 424 nm; as predicted,[9] the larger halogen atoms generate a greater distortion of the porphyrin, thereby producing a smaller HOMO-LUMO

gap. Porphyrin saddling also is responsible for the red shifts of the Q(0,1) bands of RuTFPPX$_8$ complexes from those of the corresponding TPP derivatives (Figure 3.7 and 3.8).

Relatively weak bands at 670 ($\varepsilon \approx 800$) and 792 nm ($\varepsilon \approx 300$ M^{-1}cm^{-1}) are observed in the spectrum of RuTFPPCl$_8$(py)$_2$ (Figure 3.10). Low-lying Ru$^{II} \rightarrow$ eπ^* (TFPPCl$_8$) transitions are expected, since the electrochemical data show that both Ru^{II} oxidation and TFPPCl$_8$ reduction are accessible. Extensive backbonding to eπ^* (TFPPCl$_8$) orbitals would stabilize d$_{xz}$, d$_{yz}$ relative to d$_{xy}$ (Figure 3.6); it is likely, then, that a d$_{xy}$ electron is involved in both electrochemical and the 792-nm spectroscopic oxidation of Ru^{II} to Ru^{III}. No bands above 650 nm were observed in the spectrum of RuTFPPCl$_8$(CO), consistent with the absence of any Ru^{II} oxidations in the electrochemical experiments. The dπ orbitals for RuTFPPCl$_8$(CO) are anticipated to fall at a similar energy as the porphyrin b$_2$ π orbital. Any charge transfer band in this region would be obscured by the intense porphyrin $\pi \rightarrow \pi^*$ transition. However, a b$_2$ d$\pi \rightarrow$ eπ^* transition may be contributing to the slight tailing on the low energy side of the Soret band of RuTFPPCl$_8$(CO).

Spectroelectrochemistry was performed to confirm the assignment of the LUMO as metal or ligand based in the ruthenium porphyrins. Reduction of RuOEP(CO)[34] and RuTPP(CO)[35] has demonstrated distinct differences in the UV-Vis depending on the site of reduction. Formation of a radical porphyrin anion is accompanied by a broadening of the Soret, with a concomitant decrease in intensity. The Q bands disappear, and a new band around 600 - 700 nm grows into the spectrum. RuOEP(CO)(THF)[34] and RuTPP(CO)[35] in THF both show these type of spectral features upon reduction. Reduction of RuTFPPCl$_8$(py)$_2$ (Figure 3.11) is accompanied by a decrease in the Soret intensity, with a red shift to 420 nm, as well as a decrease in the Q band intensity. A new band appears at 580 nm, consistent with formation of a porphyrin based radical anion. Spectroelectrochemistry in a different solvent has been shown to have completely different

characteristics, indicating that the axial ligand can alter the site of reduction. Upon reduction in benzonitrile, the Soret band of RuOEP(CO) is still sharp, and shows a slight red shift. No new features are observed in the lower wavelength regions.[34] Reduction of RuTFPPCl$_8$(CO) is shown in Figure 3.12. The Soret band decreases in intensity, and shows a similar red shift as in RuTFPPCl$_8$(py)$_2$, but the broadening generally associated with radical anion formation is not observed. In addition, there is no major change in the Q-band region. Isosbestic points at 270, 376, 420, and 440 nm indicate that clean reduction is occurring, but the decrease in Soret intensity suggests that this reduction may have both metal and ligand character.

Conclusion

The distortion of the porphyrin macrocycle, as observed in the crystal structures of the halogenated free ligand, zinc, and ruthenium porphyrins (Chapter 2), gives rise to the expected red shifted optical spectra and anodically shifted electrochemistry common to porphyrins substituted with electron withdrawing ligands. Only the RuTFPPX$_8$ complexes show Soret transitions at higher energy, which has been demonstrated to stem from strong coupling between the ruthenium and porphyrin orbitals. Attempts to photolyze the carbonyl ligand further support strong interactions between these orbitals; despite a relatively high ν_{CO} (indicating a correspondingly weak Ru-C bond), it is difficult to remove the carbonyl ligand with light energy. Rather than leading to dissociation, the excited state appears to decay by non-radiative pathways. No emission is observed for either the RuTFPPCl$_8$(CO) or Ru(TFPPCl$_8$)py$_2$ complexes.

The highly positive reduction potentials of the perhalogenated ruthenium and iron complexes indicate that these compounds will be quite stable in a highly oxidizing environment. Further experiments will test to see if they display the high activity as oxidation catalysts for which they were designed.

Methods

Infrared spectra were recorded as solutions in carbon tetrachloride or benzene on a Perkin-Elmer Model 1600 FT-IR spectrophotometer. Electronic absorption spectra were recorded on an Olis-modified Cary-14 spectrophotometer. Electrochemistry was performed under Ar in three compartment cell consisting of a highly polished glassy carbon working electrode, a Ag/AgCl reference electrode in 1M KCl, and a platinum auxiliary electrode. The working electrode and reference electrode are connected by a modified Luggin capillary. Spectroelectrochemical experiments were performed in an optically transparent platinum working electrode.[36] Spectral changes were monitored with a Hewlett Packard 8452A diode array spectrophotometer. A 1000 W tungsten lamp was used for photolysis experiments.

Materials

Porphyrins were obtained as described in Chapter 2. Solvents were Omnisolv grade from EM Science, and used as received.

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Figure 3.1 -- An absorption spectrum of ZnTPP, a normal porphyrin. The Soret (or B) absorption usually lies around 410 nm, and the Q bands are at lower energy. The shoulder on the Soret has been assigned as a $\pi \rightarrow \pi^*$ transition (N band).
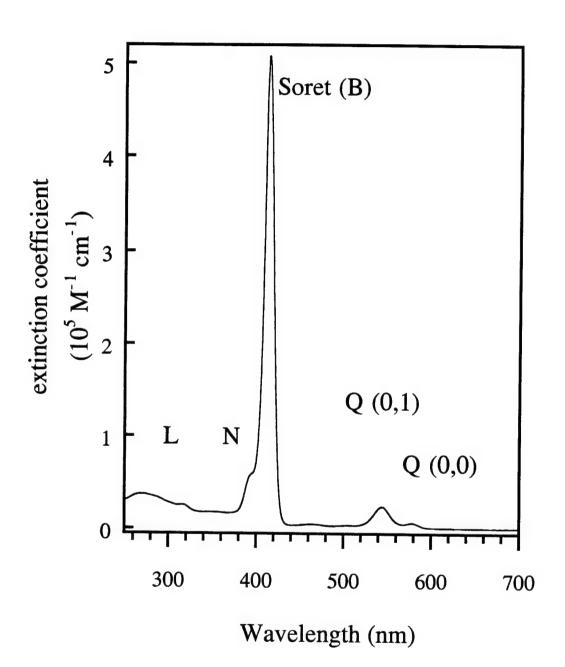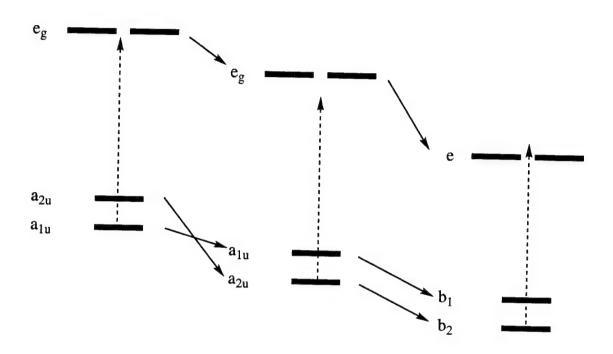
Figure 3.2 -- The Gouterman four orbital model for normal porphyrins is shown on the

left (with D_{4h} symmetry labels). Upon fluorination of the phenyl rings,

both the HOMO and the LUMO are stabilized, and the relative energy of the

a_{1u} and a_{2u} HOMOs are reversed. Halogenation of the pyrrole carbons

results in a further stabilization of all of the orbitals (pictured on the right).

The distortion of the molecule drops the symmetry to approximately D_{2d}.

The Soret transition is marked on each molecular orbital diagram with an

arrow of equal length, showing the increase in the HOMO-LUMO gap in

TFPP and the decrease in TFPPCl$_8$.

Gouterman Four Orbital Model

Figure 3.3 -- The UV-Vis spectra of the ZnTPP series of porphyrins in methylene

chloride. As shown in the molecular orbital diagrams in Figure 3.2, the

energy of the Soret transition decreases as ZnTFPP > ZnTPP > ZnTFPPCl$_8$

> ZnTFPPBr$_8$.
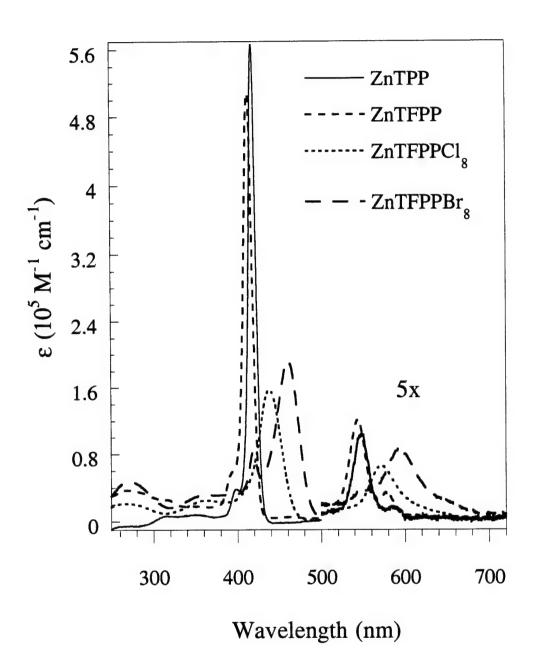
Figure 3.4 -- The UV-Vis spectra of Fe(TFPP)Cl and Fe(TFPPBr$_8$)Cl in methylene chloride. The LMCT of Fe(TFPPBr$_8$)Cl mixes with the Soret band, increasing the extinction coefficient of this transition relative to the 350 nm band in Fe(TFPP)Cl.
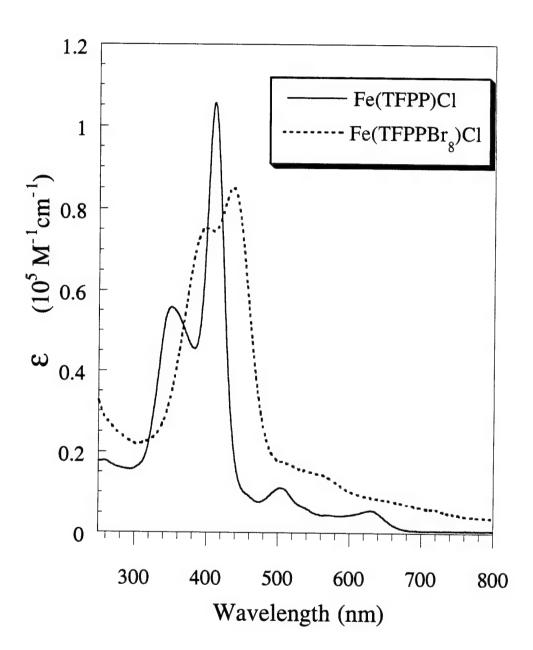
Figure 3.5 -- The UV-Vis spectra of [Fe^{II}(TFPPBr$_8$)Cl]$^-$ and [Fe^{II}(TFPPBr$_8$)(OCH$_3$)$_2$]

produced by bulk electrolysis or chemical reduction in methylene chloride.

The red shifted Soret band and the single Q band are consistent with

formation of an iron(II) porphyrin. The axial ligands for the two complexes

are determined from a combination of electrochemical data and ^{19}F NMR.
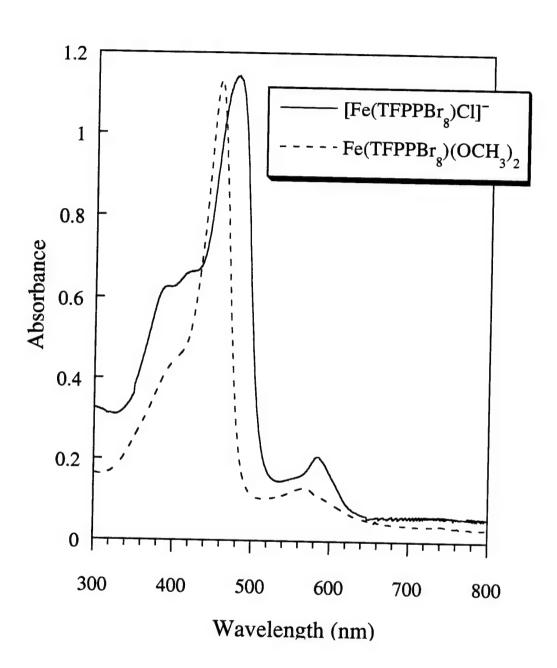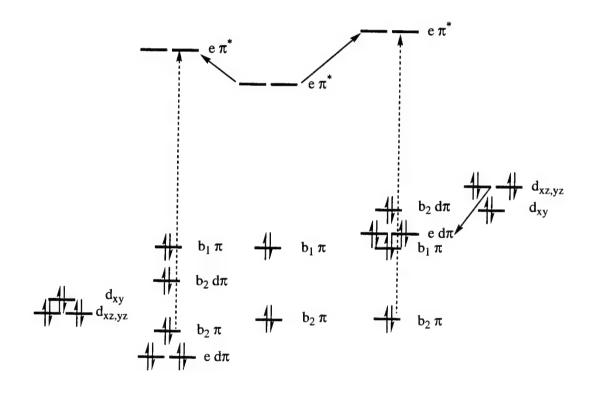
Figure 3.6 -- The Gouterman four orbital model for RuTFPPX$_8$ complexes. The

porphyrin TFPPX$_8$ orbitals are allowed to interact with the dπ orbitals of

carbonyl or bis-pyridine ruthenium fragments (D_{2d} symmetry). Extensive

π-backbonding to the carbonyl ligand strongly stabilizes the d$_{xz}$, d$_{yz}$

orbitals, resulting in a ligand based HOMO for RuTFPPX$_8$(CO). Weaker

interactions in the bis-pyridine complex leaves the dπ orbitals at higher

energies, consistent with a Ru-based HOMO and low energy charge transfer

transitions in RuTFPPX$_8$(py)$_2$. The Soret transition is shown with an

arrow for both complexes.

"Ru(CO)"   RuTFPPX$_8$(CO)   H$_2$TFPPX$_8$ RuTFPPX$_8$(py)$_2$ "Ru(py)$_2$"
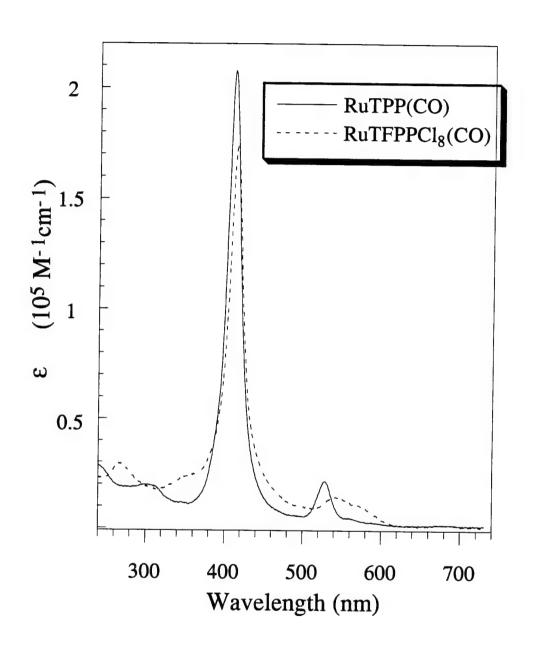
Figure 3.7 -- The UV-Vis spectra of RuTPP(CO) and RuTFPPCl$_8$(CO) in methylene

chloride. Although the Soret energy is similar for the two complexes, the

Q(1,0) transition is red shifted for the perhalogenated complex.

Figure 3.8 -- The UV-Vis spectra of RuTPP(py)$_2$ and RuTFPPCl$_8$(py)$_2$ in methylene chloride.
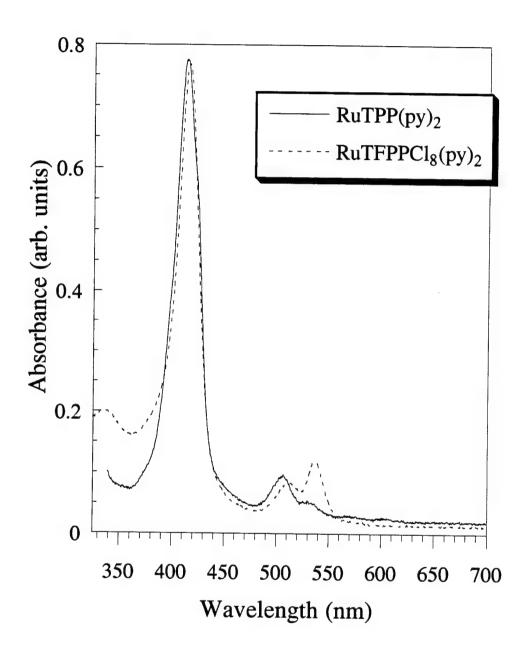
Figure 3.9 -- The UV-Vis spectra of the $RuTFPPX_n(CO)$ complexes in methylene
chloride. The Soret energy decreases with halogenation: $RuTFPPCl_6(CO)$
$> RuTFPPCl_7(CO) > RuTFPPCl_8(CO) > RuTFPPBr_8(CO)$, with the larger
bromine atoms inducing a larger red shift than chlorine. The Q bands (not
shown) show a similar change in energy.

Figure showing UV-Visible absorption spectra with legend:
- RuTFPPCl$_8$(CO)
- RuTFPPCl$_7$(CO)
- RuTFPPCl$_6$(CO)
- RuTFPPBr$_8$(CO)

X-axis: Wavelength (nm), ranging from 300 to 500.
Y-axis: Absorbance, ranging from 0 to 1.
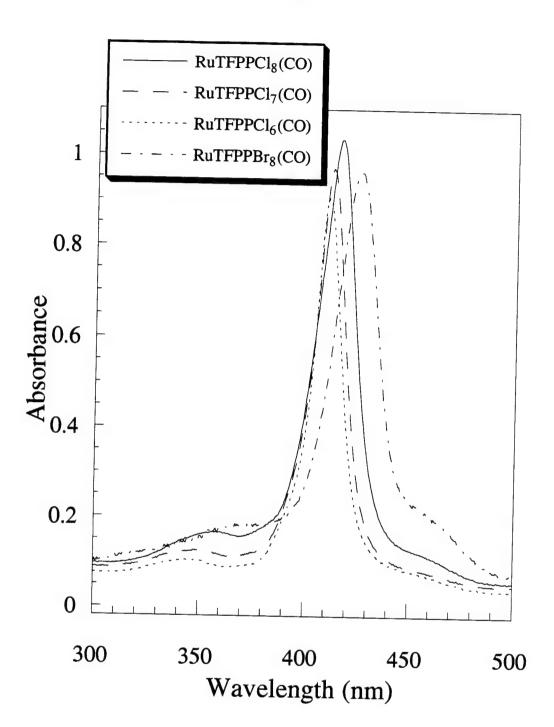
Figure 3.10 -- The low energy visible spectrum of $RuTFPPCl_8(CO)$ and

$RuTFPPCl_8(py)_2$. The two absorptions at 670 and 792 nm in the bis-

pyridine spectrum are assigned to $Ru^{II} \rightarrow e\pi^*$ ($TFPPCl_8$) transitions.

MLCT transitions in the carbonyl complex are anticipated to lie at higher

energy and are obscured by porphyrin $\pi \rightarrow e\pi^*$ transitions.
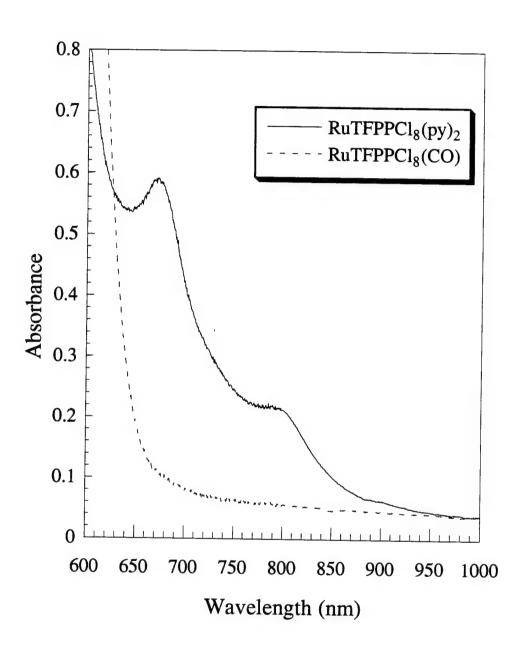
Figure 3.11 -- Spectroelectrochemical reduction of RuTFPPCl$_8$(py)$_2$ in methylene chloride. The reduced species shows clear porphyrin radical character.
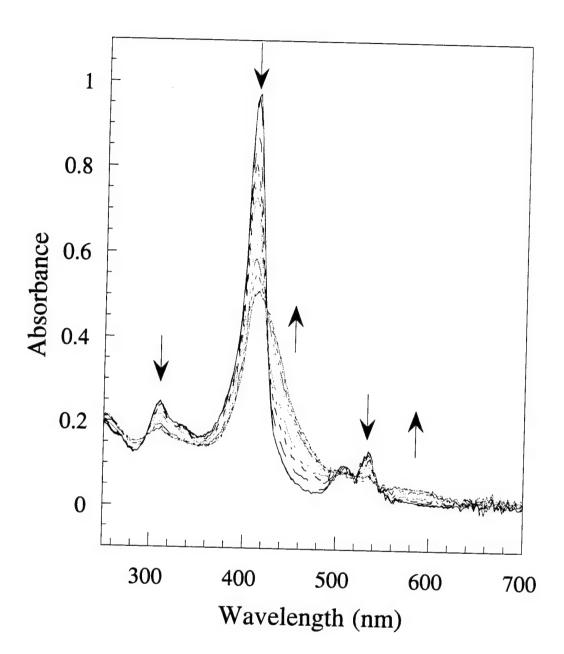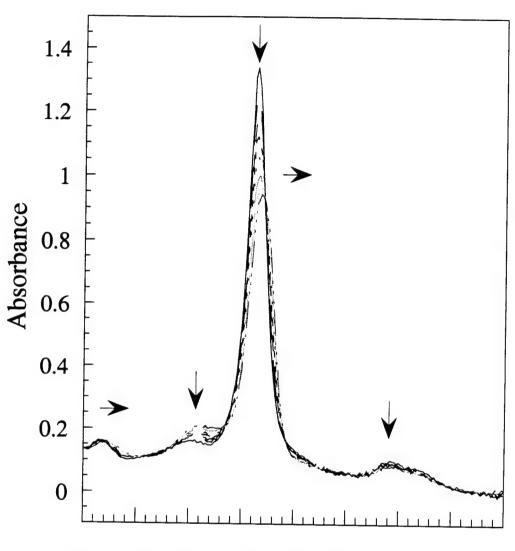
Figure 3.12 -- Spectroelectrochemical reduction of RuTFPPCl$_8$(CO) in methylene chloride. While the reduced species shows a decrease in the Soret intensity, consistent with formation of a porphyrin radical anion, no change in the Q band region is observed.

Table 3.1. Electronic Absorptions of Halogenated Porphyrins.

Porphyrin	L, M bands (ε, 10^3 M^{-1} cm^{-1})	Soret, nm (ε, 10^5 M^{-1} cm^{-1})	Q bands, nm (ε, 10^4 M^{-1} cm^{-1})			
ZnTPP	315 (1.0) 350 (1.5)	418 (5.6)	548 (2.1)			
ZnTFPP	318 (4)	413.5 (5.0)	544 (2.4)			
ZnTFPPCl$_8$	360 (3.0)	439 (1.6)	572 (1.3)			
ZnTFPPBr$_8$	364 (3.3)	460 (1.9)	594 (1.7)			
H$_2$TPP[a]		419 (4.7)	514 (1.9)	549 (0.77)	591 (0.54)	647 (0.34)
H$_2$TFPP[a]		412 (2.4)	506 (1.9)	584 (0.58)	659 (0.36)	
H$_2$TFPPCl$_8$		438 (1.6)	538 (1.3)	626 (0.46)		
H$_2$TFPPBr$_8$		454	532	636		
RuTPP(CO)	300 (20)	412 (2.0)	528 (2.1)			
RuTFPPCl$_8$(CO)	355 (25)	416 (1.7)	548 (1.4)	580 (1.0)		
RuTFPPCl$_7$(CO)	345	413	541	576		
RuTFPPCl$_6$(CO)	340	411	539	572		
RuTFPPBr$_8$(CO)	370	426	595			
RuTPP(py)$_2$		413	507	534		
RuTFPPCl$_8$(py)$_2$	355	414 (1.6)	512 (2.0)	536 (2.5)	670[b] (0.08)	790[b] (0.03)
RuTFPPCl$_7$(py)$_2$		414	510	536	672[b]	790[b]
RuTFPPCl$_6$(py)$_2$		412	508	534	674[b]	790[b]
RuTFPPBr$_8$(py)$_2$		424	518	572		

a. Extinction coefficients in benzene, from Longo, F. R.; Finarelli, M. G.; Kim, J. B. *J. Hetero. Chem.*, **1969**, *6*, 927-931.
b. Assigned as MCLT absorptions.

Table 3.2. Reduction Potentials of Halogenated Porphyrins.

Porphyrin[a]	$E''_{+/0}$	$E''_{M(III)/M(II)}$	$E''_{0/-}$
ZnTPP[b]	0.80	—	-1.33
ZnTFPP[b]	1.37	—	-0.95
ZnTFPPCl$_8$[b]	1.60[c]	—	-0.76
ZnTFPPBr$_8$[b]	1.55[c]	—	-0.75
H$_2$TPP[d]	1.08	—	-1.21
H$_2$TFPP	1.53	—	-0.78
H$_2$TFPPCl$_8$	1.66[e]	—	-0.32
H$_2$TFPPBr$_8$	1.56[e]	—	-0.31
RuTPP(CO)[f]	0.86		-1.46
RuTFPPCl$_6$(CO)	1.64	—	-0.76
RuTFPPCl$_7$(CO)	1.69	—	-0.69
RuTFPPCl$_8$(CO)	1.71	—	-0.64
RuTFPPBr$_8$(CO)	1.63	—	-0.84
RuTPP(py)$_2$[d]	—	0.21	—
RuTFPPCl$_6$(py)$_2$	—	0.89	-1.12
RuTFPPCl$_7$(py)$_2$	—	1.04	-0.98
RuTFPPCl$_8$(py)$_2$	—	1.08	-0.94
Fe(TPP)Cl[g]	1.14	-0.29	-1.07
Fe(TFPP)Cl	1.65	-0.08	-1.10
Fe(TFPPBr$_8$)Cl	—	0.31	-0.63

a. Potentials in CH_2Cl_2 solution at room temperature (V vs. AgCl/Ag, 0.1M TBAPF$_6$).
b. The zinc potentials are from reference 13.
c. $E''_{2+/0}$.
d. V. vs SCE in 0.05M THAP. From reference 12.
e. E_{pa}.
f. V. vs. SCE in 0.1 M TBAP in CH_3CN. From reference 29.
g. From reference 26.

Table 3.3. Electronic Absorptions of Halogenated Iron Porphyrins.

Porphyrin	L, M bands	Soret, nm (ε,10^5 M^{-1} cm^{-1})	Q bands, nm (ε, 10^4 M^{-1} cm^{-1})		
Fe^{III}(TPP)Cl[a]		419 (1.7)	510 (1.2)	573 (0.037)	656, 692 (0.028, 0.32)
Fe^{II}(TPP)Cl[a]		444 (1.7)	530 (0.32)	571 (0.75)	612 (0.65)
Fe^{III}(TFPP)Cl		411 (1.0)	351 (0.70)	504 (1.1)	621 (0.56)
"Fe^{II}(TFPPCl$_8$)"[b]	398	440	566		
Fe^{III}(TFPPBr$_8$)Cl	404 (0.81)	440 (0.85)	560 (2.0)		
[Fe^{II}(TFPPBr$_8$)Cl]$^-$	388, 420	478	585		
Fe^{II}(TFPPBr$_8$)(OMe)$_2$		454	568		
Fe(TPP)py$_2$					
Fe(TFPP)py$_2$		418	525	552	
Fe(TFPPCl$_8$)py$_2$		438	542	574	
Fe(TFPPBr$_8$)py$_2$		452	556	588	
(FeTFPP)$_2$O[c]		398 (0.62)	577 (0.7)	590 (sh)	
Fe(TFPP)OH[c]		406 (7.6)	563 (1.2)		

a. Spectra taken in PhCN; from reference 8.
b. Appears to be iron (II) based on the red color. See text.
c. Extinction coefficients from reference 40, Chapter 2.

Chapter 4

Mechanism of Catalytic Alkene Oxidation with Molecular Oxygen or Iodosobenzene and Halogenated Iron Porphyrins

Introduction

Since the discovery that tetraphenylporphyrinato-iron(III) chloride [Fe(TPP)Cl] catalyzes olefin epoxidation with iodosobenzene,[1] a variety of porphyrins have been tested for the ability to mediate hydrocarbon oxidation reactions utilizing assorted oxygen sources.[2] These studies have generally striven to generate high-valent metal-oxo intermediates to mimic the putative active species in cytochrome P-450. Most experiments take advantage of the peroxide shunt pathway to directly form the desired metal-oxo species, while reactions with dioxygen are usually carried out in the presence of a reductant to follow the complete P-450 oxygen activation mechanism.

The reaction of iodosobenzene (PhIO) with metalloporphyrins has been well documented.[1,3-8] The iodosobenzene polymer oxidizes $M^{III}(P)X$ complexes to $M^V(P)(O)$ species as shown in Eq. 1, where P = porphyrin, X = halide, ^-OH, etc., R = phenyl, and R' is the continuing iodosobenzene polymer.[9] Some evidence also exists for the transient

$$
\overset{|}{\underset{|}{M}}{}^{III} + R\text{-}I\overset{OH}{\underset{OR'}{}} \; \underset{}{\overset{K_{eq}}{\rightleftharpoons}} \; \overset{|}{\underset{|}{M}}{}^{III}\text{-}O\text{-}I\overset{H \quad R}{\underset{+ \quad OR'}{}} \; \xrightarrow{\;k\;} \; \overset{|}{\underset{|}{M}}{}^V{=}O \;+\; RI + R'OH \quad (1)
$$

formation of a μ-oxo dimer intermediate, $(P)M^{IV}\text{-}O\text{-}M^{IV}(P)^{\bullet+}$, formed from a reaction of $M^V(P)(O)$ with another porphyrin molecule.[10,11]

Whether the last oxidizing equivalent is more appropriately characterized as a M^V or as a $M^{IV}(P^{+\bullet})$ depends on the metal and porphyrin involved. Spectroscopic evidence indicates that most iron porphyrins are oxidized to form porphyrin radical cations,[12-14] as does the heme center in the enzyme horseradish peroxidase (HRP) The high-valent metal-oxo of HRP (compound I) is well characterized as $Fe^{IV}(P^{+\bullet})(O)$ and is often used as a standard for comparisons with model complexes.[15] Oxidation of $Fe^{III}(TMP)Cl$ with

m-chloroperbenzoic acid (mCPBA) at -77 ˚C is reported to give UV-Vis and ^{1}H NMR spectra consistent with formation of an iron(IV) porphyrin π-radical cation.[14] EXAFS and Mössbauer spectra are similar to those of HRP compound I, further supporting this assignment.[16] With other metals, such as chromium, the last electron is removed from a metal based orbital.[17] For Cr[III]TPPCl, UV-Vis and IR spectroscopy, in combination with magnetic susceptibility measurements, indicate formation of Cr[V]TPP(O) upon oxidation with mCPBA or PhIO.[18]

Once the high-valent metal-oxo is generated, there are a number of mechanisms for interaction with an olefin. Possible intermediates include a metallaoxetane (I), a π-radical cation (II), a carbocation (III), a carbon radical (IV), or a process of concerted oxene insertion (V) (Figure 4.1).[19] The metallocyclo intermediate has been excluded, especially for sterically encumbered porphyrins, since modeling demonstrates that the reaction coordination sphere is not large enough to accommodate formation of the four-membered ring.[20,21] Although many elegant experiments have been conducted to further probe the transition state, there is no consensus indicating a general metalloporphyrin oxidation mechanism. The academically unsatisfying conclusion seems to be that the mechanism is dependent on the metal ion and the electron density of the porphyrin and alkene substrate.[19]

Nevertheless, a few general concepts concerning the mechanism have been proposed (Figure 4.2).[17,21-23] The first step has been proposed to be association of the metal-oxo and the olefin, in some cases called a charge transfer (CT) complex. With Cr[V](TDBPP)(O) (TDBPP = tetrakis-(2,6-dibromophenyl)porphyrin), the formation of this complex is rate limiting,[17] and other evidence suggests this is also true for the iron derivative. The reaction of Fe(TMP)Cl with mCPBA and cyclooctene at -43 ˚C resulted in an observable intermediate prior to epoxide formation, again suggested to be an olefin π-complex.[13] The charge transfer complex may then react through various pathways, including concerted oxene transfer (V), electrophillic addition (III), or electron

transfer (IV).[19-21] The relative rates for each pathway are determined in each case by the electron density on the olefin and the electrochemical potential of the metal center. Unfortunately, the actual oxo transfer step is after the rate limiting formation of the CT complex, precluding its direct observation.

For the specific case of cyclohexene oxidation, different pathways are implicated for hydroxylation and epoxidation (Figure 4.3). Oxidation of deuterated cyclohexene with Fe(TPP)Cl and Cr(TPP)Cl has shown that allylic oxidation occurs via allylic hydrogen atom abstraction followed by geminate radical recombination.[24] Further experiments with partially halogenated porphyrins supported this mechanism for hydroxylation[25] and suggested that formation of cyclohexene epoxide occurs by direct electron transfer to form a carbocation intermediate (Figure 4.3). Competition between direct hydrogen abstraction and electron transfer depends on the electron density at the metal, allowing for different selectivity as observed with different metals.[25] The higher selectivity for epoxidation observed with electron-withdrawing iron porphyrins suggests that the higher reduction potential favors the electron transfer mechanism.[25] Correlations of epoxidation rates with the reduction potential or the Hammett parameter of the olefin have also been argued to support an electron transfer mechanism for Fe(TDCPP)Cl.[26]

The perhalogenated porphyrin, 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetrakis(pentafluorophenyl)porphyrinato-iron(III) chloride, [Fe(TFPPBr$_8$)Cl], is an active catalyst for the selective oxidation of light alkanes at elevated temperatures (80 ˚C) and under high dioxygen pressure (80 atm).[27,28] Recently, we reported that at room temperature and one atmosphere of molecular oxygen, Fe(TFPPBr$_8$)Cl will oxidize 3-methylpentane to 3-methylpentan-3-ol.[29] We have now found that this metalloporphyrin is also an efficient catalyst for the oxidation of cyclohexene with either dioxygen or single O-atom donors such as iodosobenzene.

Results

In the presence of Fe(TFPPBr$_8$)Cl, cyclohexene oxidation to a mixture of cyclohexene oxide, 2-cyclohexen-1-ol, and 2-cyclohexen-1-one, was observed (Figures 4.4 and 4.5). The product distribution and activity varied greatly with the oxidant. With PhIO, the majority of product (77%) consisted of the epoxide. With dioxygen, mainly allylic oxidation products were generated (49 and 44% of alcohol and ketone, respectively). Reactions with styrene exhibited similar differences in product distribution with oxidant. With PhIO, the majority of the product (67%) was styrene oxide, while with dioxygen, only the cleavage product, benzaldehyde (> 95%), was observed.

Catalytic activity also varied with oxidant. Iodosobenzene reactions deactivated in 1 to 5 hours, accompanied by a shift in the Soret band from 442 to 418 nm. However, 18 ± 4 turnovers (TO) were completed during this time period, and the product distribution (Figure 4.4) was consistent between runs. Although the initial activity with PhIO was greater, overall activity was higher with dioxygen, suggesting an induction period for the latter reaction. Furthermore, in reactions with dioxygen, the perhalogenated porphyrin showed much higher activity at 24 hours (73 TO) as compared to the related porphyrins tetrakis(pentafluorophenyl)porphyrinato-iron(III) chloride (Fe(TFPP)Cl) (31 TO) and tetraphenylporphyrinato-iron(III) chloride (Fe(TPP)Cl) (< 1 TO) (Figure 4.6).

The variations in selectivity with Fe(TFPPBr$_8$)Cl can be explained by invoking different mechanisms for the two oxidants. Iodosobenzene is believed to react with metalloporphyrins to generate a high-valent metal-oxo intermediate, as described above.[30] Indeed, the large percentage of epoxide formed with PhIO and Fe(TFPPBr$_8$)Cl is consistent with a ferryl as the oxidizing species. The increase in activity from Fe(TFPPBr$_8$)Cl relative to Fe(TFPP)Cl, however, is not as great as one might predict: the positive E° Fe$^{3+/2+}$ (0.31 V vs. AgCl/Ag)[29] of the perhalogenated porphyrin would make an "Fe^V=O" of this porphyrin high in energy and difficulty to attain.[23] In line with

this prediction, reductive generation of a ferryl (O_2, Zn, H^+) has been shown to be inefficient for highly halogenated porphyrins.[31,32] The lower potentials of Fe(TFPP)Cl (-0.08 V)[29] and Fe(TPP)Cl (-0.29 V vs. SCE)[33] suggest that a ferryl complex can be generated more readily in these complexes. However, once formed, the ferryl can attack the C-H bonds on other porphyrins, leading to catalyst decomposition and lower net activity with these two complexes.

With dioxygen, the formation of a metal-oxo is not observed. Previously in the literature,[34] the active species was proposed to be (P)Fe^{IV}=O, formed by reaction of dioxygen with (P)Fe^{II} to form a μ-peroxy bridged dimer (Figure 4.7). Homolytic cleavage of the dimer to (P)Fe^{IV}=O would result in dioxygenase-type oxygen activation.[27,34,35] With electron-withdrawing porphyrins, it was proposed that an iron(IV)-oxo would have as much oxidizing power as a typical iron(V)-oxo porphyrin. Although the positive reduction potential of Fe(TFPPBr$_8$)Cl is consistent with this mechanism, the increased stability of the ferrous state causes both the iron(II) and iron(III) oxidation states to be stable to oxygen. A solution of electrochemically generated [Fe^{II}(TFPPBr$_8$)Cl]$^-$ only shows minimal oxidation after several weeks under an O_2 atmosphere,[36] indicating that this pathway is not operative.[29] Attempts to generate an iron(IV)-oxo directly, by addition of iodosobenzene to electrochemically produced [Fe^{II}(TFPPBr$_8$)Cl]$^-$ in methylene chloride, resulted only in immediate conversion to Fe^{III}(TFPPBr$_8$)Cl.

The possibility of reductive ferryl generation with Fe(TFPPBr$_8$)Cl is eliminated for several reasons. First, the lack of an added co-reductant allows no mechanism for the reduction of the ferric porphyrin to the ferrous state. Furthermore, [Fe^{II}(TFPPBr$_8$)Cl]$^-$ is stable to dioxygen, meaning that the oxygen binding step from the P-450 cycle does not occur. As mentioned above, reductive ferryl generation has been shown to be inefficient for halogenated iron porphyrins,[31,32] suggesting that a high-valent metal-oxo is not

implicated in reactions of Fe(TFPPBr$_8$)Cl with dioxygen. A mechanism less common to metalloporphyrins must be investigated.

Indeed, the reaction has been shown to involve formation and porphyrin-catalyzed decomposition of alkyl peroxides (Figure 4.8).[29,37] Free radicals present in solution react with oxygen to form alkyl peroxides. The alkyl peroxides, unlike dioxygen, react more readily with highly electron-deficient porphyrins such as Fe(TFPPBr$_8$)Cl (*vide infra*). The radicals generated by the Fe(TFPPBr$_8$)Cl-catalyzed peroxide decomposition react with additional molecules of substrate to form the observed products, propagating a radical chain reaction. A plot of moles product produced versus time (Figure 4.5) indicates that the reaction is autocatalytic. Competitive experiments with cyclohexene and cyclohexene-d_{10} show an isotope effect of 8.2, consistent with a mechanism involving hydrogen abstraction in the rate-determining step. Addition of a radical trap, BHT, completely inhibits the reaction. The radical chain mechanism is also consistent with the high percentage of allylic oxidation products observed in the reaction of cyclohexene with dioxygen.

Moreover, this mechanism explains the greater reactivity observed with dioxygen and Fe(TFPPBr$_8$)Cl compared to tetraphenylporphyrinato-iron(III) chloride or tetrakis(pentafluorophenyl)porphyrinato-iron(III) chloride. The electron-withdrawing TFPPBr$_8$ ligand stabilizes the ferrous state, thereby enhancing the rate of alkyl peroxide oxidation.[36] In contrast, the lower reduction potentials of Fe(TFPP)Cl and Fe(TPP)Cl make these species poor oxidants, greatly slowing the ferric $\rightarrow$ ferrous step in the catalytic cycle. Furthermore, as with ferryl complexes, any radicals generated in the presence of Fe(TFPP)Cl or Fe(TPP)Cl may decompose the porphyrin by attacking C-H bonds. Halogenation of the β positions of the porphyrin is also believed to prevent formation of a μ-oxo dimer,[29,35] which is a mode of deactivation for both Fe(TPP)Cl and Fe(TFPP)Cl in reactions with dioxygen.[38] Thus the perhalogenated porphyrin has a faster rate of catalysis but a lower rate of catalyst degradation in solution

In order to further explore the possibility of an active iron(IV) or iron(V) oxo species, the synthesis of $Fe^{III}(TFPPBr_8)OH$ was attempted. Either chemical oxidants or bulk electrolysis could be used to generate a high-valent metal-oxo from an iron(III) hydroxide porphyrin. The pentafluorophenyl derivative, Fe(TFPP)OH, has been produced by washing Fe(TFPP)Cl with NaOH in benzene.[39] Instead, we attempted to isolate the hydroxide salt directly from the iron insertion reaction. As described in Chapter 2, $Fe^{II}(OAc)_2$ in glacial acetic acid inserts into $H_2TFPPBr_8$. The red color and red shifted Soret band of this species (in situ, $\lambda_{max} = 448$ and 578 nm) are consistent with formation of $Fe^{II}(TFPPBr_8)(OAc)_2$. Instead of brine, a weak sodium hydroxide solution was used to quench the metal insertion reaction, which would provide a hydroxide ligand for the iron ion. The porphyrin that precipitated from the reaction was filtered and washed with water; the absorption spectrum of resulting solid has a maximum at 434 and a Q band at 584 nm. The blue shift from Fe(TFPPBr$_8$)Cl, as well as the shape of the spectrum, is analogous to the change from Fe(TFPP)Cl to Fe(TFPP)OH, suggesting formation of Fe(TFPPBr$_8$)OH. Purification by column chromatography resulted in a new species, with a Soret at 418, a strong shoulder at 486, and a Q band at 600 nm. This species had the same spectrum as Fe(TFPPBr$_8$)Cl after 48 hours in a methylene chloride/PhIO solution, and may be the μ-oxo dimer. The blue shift of the Soret band and red shift in the Q bands is again the same as observed in the TFPP complexes. Although modeling has suggested that formation of [Fe(TFPPBr$_8$)]$_2$O is unfavorable due to poor steric interactions, a weak complex may form. Rather than becoming a permanently unreactive species, however, this dimer may be able to break apart and undergo further reactions, as has been suggested for (FeTFPP)$_2$O.[40] An alternative explanation of catalysis with a μ-oxo dimer is that dimerization *protects* one side of the porphyrin ligand, allowing oxidation to occur on the opposite side.[41] Attempts to obtain a ^{19}F NMR of this material were unsuccessful, and due to the small amounts of compound obtained, this chemistry was not further pursued.

Conclusion

Fe(TFPPBr8)Cl is a remarkably active catalyst for the oxidation of cyclohexene with dioxygen, without added coreductant or light. The mechanism does not involve traditional high-valent metal-oxo intermediates, but interacts through the lower oxidation states of the porphyrin. Catalytic oxidation and reduction of alkyl peroxides by Fe(TFPPBr8)Cl generates radicals that continue free-radical chemistry in solution.

Other than halogenated porphyrins, only the highly activated porphyrin RuTMP(O)$_2$ [dioxo(tetramesitylporphyrinato)-ruthenium(VI)] is known to catalyze the aerobic epoxidation of alkenes at ambient temperatures and pressures. Although able to catalyze 26 turnovers of cyclooctene in 24 hours (versus 73 TO of cyclohexene by Fe(TFPPBr8)Cl), the Ru catalyst decomposes within this time period.[42] Another electron-deficient porphyrin, β-hexanitro-tetrakis(2,6-dichlorophenyl)porphyrinato iron (III) chloride, has been shown to activate alkanes at higher temperatures and high pressures of O$_2$.[43] Considering the similarity of the two porphyrins, it is likely that they operate by the same peroxide decomposition mechanism. Unfortunately, the exceptional reactivity of Fe(TFPPBr8)Cl with dioxygen appears to come at the expense of the selectivity found with high-valent metal-oxo species.

Methods

Oxidation reactions were run as follows. 3-4 mg of porphyrin (approximately 2-3 μmol) were added to a clean, oven-dried reaction vessel with a stir bar. For iodoso-benzene experiments, 20-30 mg of PhIO were also weighed out into the flask (~ 50 eq PhIO/Fe). The reaction vessel was then fully assembled (Figure 4.9) and flushed from the top with Ar (for PhIO reactions) or O$_2$, allowing gas to escape through the open stopcock. 15 mL freshly distilled methylene chloride (under Ar or saturated with dioxygen) was added by syringe into the reaction vessel, followed by 1 mL of freshly

distilled substrate. From the solubility of oxygen in methylene chloride and the volume of the flask, the dioxygen reactions were calculated to have approximately 1240 μmol of O_2, or ~ 450 equivalents based on iron. The Kontes valve and stopcock were then closed, isolating the flask from the external atmosphere. The reactions were stirred for the next 24 - 48 hours, and aliquots taken by syringe every few hours for analysis of oxidation products.

The reactions were carried out in special flasks designed to minimize evaporation from the vessel during a reaction. A stopcock was attached to the side of a 25 mL Kjeldahl flask as shown in Figure 4.9. A hose could be attached to one of the two tubes on the stopcock, such that sample aliquots were not exposed to oxygen, and additional air did not leak into the flasks when an aliquot was removed. Unfortunately, this method prohibited clean kinetic measurements, since the concentration of oxygen in the flask at any given time was unknown. However, the rather excessive caution in sealing the flask was found to be necessary, since experiments run in round bottom flasks sealed only with a rubber septum had evidence of significant evaporation and/or leakage. Even with these precautions, the reaction volume decreased due to evaporation of the volatile solvent, and measurement reliability decreased significantly after 24 hours.

Gas chromatography was performed on a Hewlett Packard with a SD 1 column. Samples were identified by retention times relative to authentic samples. An internal standard (toluene) was added to each aliquot before injection in the GC and used to determine the concentration of each product.

Materials
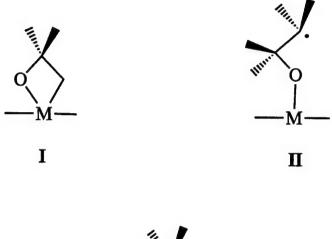
Porphyrins were obtained as described in Chapter 2. Iodosobenzene was purchased from TCI. Some batches were rather yellow in color, and were washed with benzene to remove impurities, with only some success. Methylene chloride, styrene, cyclohexene, *tert*-butyl hydroperoxide, and GC standards were purchased from Aldrich.
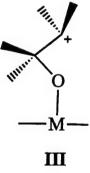
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Figure 4.1 -- Intermediates that have been proposed in the literature for epoxidation by a high-valent metal-oxo. The metallaoxetane (I) and carbon radical (II) have been ruled out by recent experiments (see text), although this is not universally accepted. The carbocation (III) and carbocation radical (IV) are still considered viable intermediates, as is concerted oxygen insertion (V).

I

II

III

IV

V
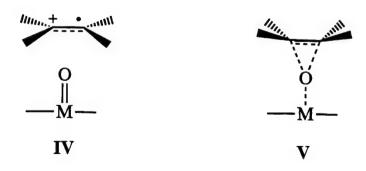
Figure 4.2 -- A proposed mechanism for epoxidation where the rate limiting step involves association of the olefin with the metal-oxo to form a charge transfer complex (CT). The CT can form an epoxide by concerted oxygen insertion, electrophillic addition, or electron transfer (shown from left to right). The carbocation radical (IV) can either recombine and form an epoxide, or continue on a radical pathway leading to hydroxylation or other rearrangement products. Mechanism modified from reference 19.

(Porphyrin)M^V=O + alkene

rate limiting

(Porphyrin)M^V=O ‧‧‧‧‧‧ alkene (CT complex)

concerted

electrophillic
addition

1e⁻ oxidation

epoxide +
rearrangment products

radical chain
products
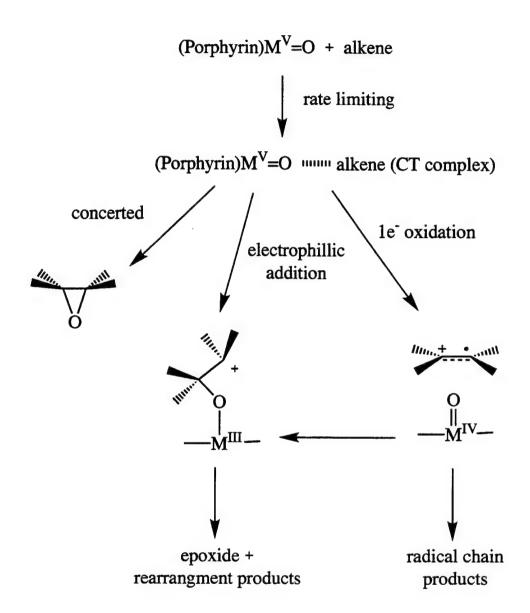
Figure 4.3 -- Multiple pathways are believed to be responsible for epoxidation and
hydroxylation of cyclohexene. Hydroxylation is generally believed to occur
via hydrogen abstraction. In addition to the electron-transfer epoxidation
mechanism shown, direct oxygen insertion may also occur. The branching
ratio is dependent on the nature of the olefin, the porphyrin, and the solvent.
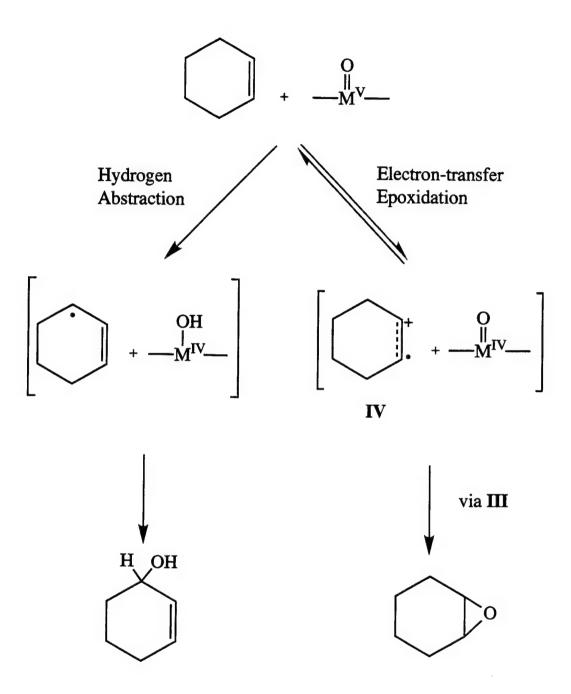
Figure 4.4 -- Turnovers and product distributions with cyclohexene and iron(III) porphyrins with dioxygen (at 3 hours) and PhIO (at 4 hours).
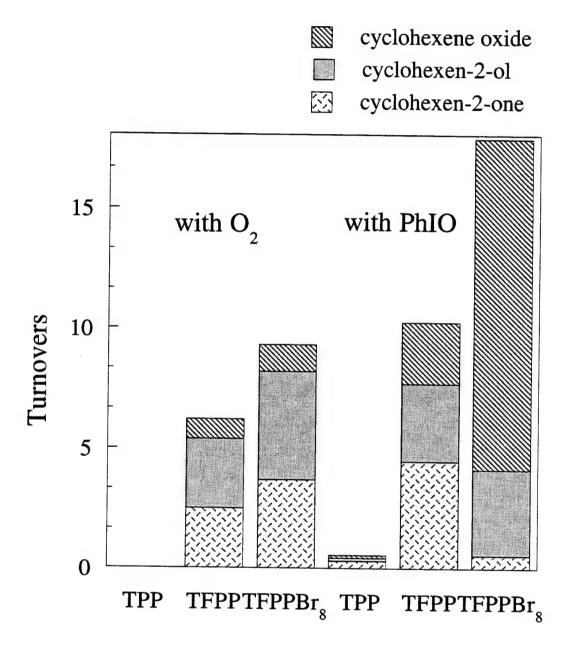
Figure 4.5 -- Product formation during cyclohexene oxidation with Fe(TFPPBr$_8$)Cl and dioxygen. The curvature of the plot indicates the autocatalytic nature of the reaction.
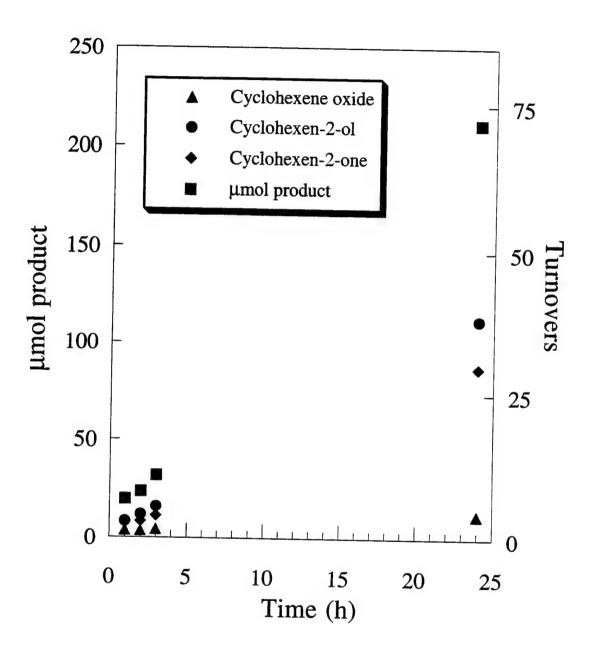
Figure 4.6 -- A plot of the catalytic activity (turnovers at 24 hours) observed for cyclohexene oxidation with dioxygen versus the reduction potential of the iron(III)-porphyrin catalyst (E° values: Fe(TPP)Cl < Fe(TFPP)Cl < Fe(TFPPBr$_8$)Cl).
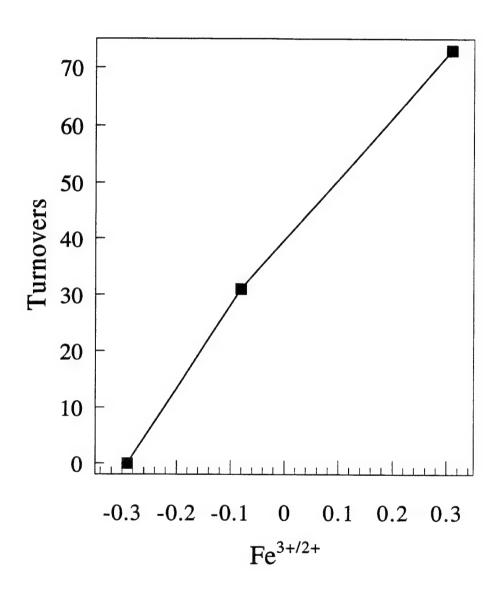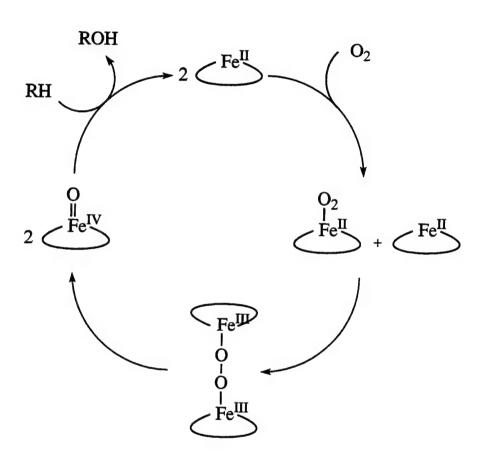
Figure 4.7 -- A proposed mechanism for direct activation of dioxygen initiated by

oxygen binding to a ferrous porphyrin (modified from reference 34). The

positive electrochemical potential ($Fe^{2+/3+}$) of the halogenated iron

porphyrins were proposed to generate an iron(IV) oxo of comparable

activity to that of a biological iron(V) oxo.

$$\bigcirc\!\!\!-\!\!\!Fe^{II}\!\!\!\rangle = Fe^{II}(TFPPBr_8)$$

Figure 4.8 -- The alkyl peroxide decomposition mechanism for dioxygen reactions with Fe(TFPPBr$_8$)Cl. Initiated by radicals in solution, the peroxides thereby generated are catalytically decomposed by the iron porphyrin. These radicals can further propagate the reaction.

Initiation by radicals
present in solution.

$$R\bullet + O_2 \longrightarrow ROO\bullet$$

$$ROO\bullet + RH \longrightarrow ROOH + R\bullet$$

RH

RO• + ⁻OH   PFe^{III} ROOH   R•

ROOH   PFe^{II} H$^+$ + ROO•   RH

ROH + R•   O$_2$ O$_2$

$$ROO\bullet + RO\bullet \longrightarrow \text{free radical propigation}$$
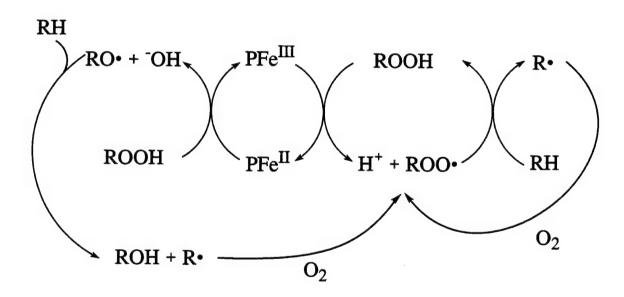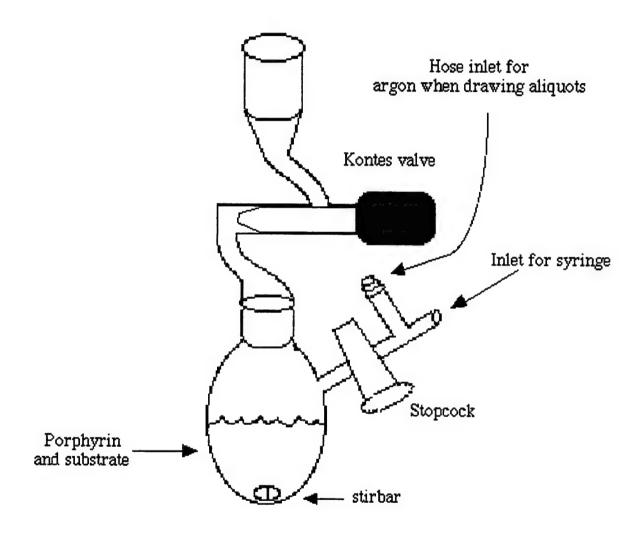
Figure 4.9 -- The modified Kjeldahl flask used for oxidation reactions. The porphyrin
and iodosobenzene are added dry, then solvent and substrate are added.
Aliquots can be removed without exposing the sample to air.

$24/40 Joint,
Could evacuate on a vacuum line
or flush with argon or dioxygen.

Hose inlet for
argon when drawing aliquots

Kontes valve

Inlet for syringe

Stopcock

Porphyrin
and substrate

stirbar

Chapter 5

On the Mechanism of Alkene Oxidation
by Ruthenium Porphyrins and Molecular Oxygen

Introduction

As described in the preceding chapter, iron tetraphenylporphyrin derivatives are catalysts for the oxidation of alkenes and alkanes with oxygen donors. A smaller number of ruthenium porphyrins have also been synthesized to further explore biomimetic metalloporphyrin oxidation chemistry. Although a few have been investigated as oxidation catalysts, a greater portion of work has focused on using ruthenium porphyrins as model complexes for iron porphyrins or as systems for dihydrogen or dinitrogen activation. For example, cofacial ruthenium porphyrin dimers have been shown to bind dihydrogen in the core between the two porphyrin molecules.[1]

Ruthenium porphyrins are commonly isolated as six-coordinate Ru^{II}(porphyrin)L_2 species with $2e^-$ donor ligands such as pyridine or CO as compared to five-coordinate Fe^{III}(porphyrin)X complexes. Greater ligand field stabilization energy for the second row metal and π bonding from π acid ligands give ruthenium(II) porphyrins greater stability relative to iron hemes.[2] This increase in stability is exploited for mechanistic investigations, as intermediates in ruthenium oxidation reactions, such as (P)Ru^{IV}=O, can be isolated and better characterized than the corresponding iron porphyrin species. Furthermore, comparisons of iron, ruthenium, and osmium porphyrin spectroscopy have been useful in determining orbital energies in iron porphyrin compounds.[3-9]

Ruthenium tetramesitylporphyrins have been investigated as catalysts for the oxidation of hydrocarbons. Groves[10] found that RuTMP(CO) is oxidized to Ru^{VI}TMP(O)$_2$ with two equivalents of m-chloroperoxybenzoic acid (mCPBA). This species is moderately stable, and has been characterized by NMR, elemental analysis, and

UV-Vis spectroscopy. The ruthenium dioxo porphyrin complex is a competent stoichiometric oxidant of norbornene, resulting in 1.6 equivalents (eq) norbornene oxide per mole of porphyrin and a solvated $Ru^{II}TMP$ complex.[11] Transfer of the first oxygen occurs more readily than the second, indicating that the monooxo complex is not as effective an oxo transfer agent as the dioxo complex.[12] However, various N-oxides have been used as O-atom donors with $Ru^{VI}TMP(O)_2$ to catalytically oxidize alkenes[13,14] and alkanes[15] in good yields (30-90% based on N-oxide).

The carbonyl complexes RuTMP(CO), RuTPP(CO), RuOEP(CO) and RuTDFPP(CO) (TDFPP = 2,6-difluororphenylporphyrin) are also observed to catalyze hydrocarbon oxidation.[15,16] With *tert*-butyl hydroperoxide (TBHP) or sodium hypochlorite as the oxidant, over 100 turnovers of styrene in 24 hours are reported for RuTDFPP(CO), and even higher activity was reported with RuOEP(CO).[16] RuTMP(CO) and RuTPP(CO) do not show activity until addition of strong acid to the solution; once activated, both porphyrins catalyze the oxidation of adamantane with 2,6-dichloropyridine N-oxide. Activity is higher when the dioxo complex is used.[15] No mechanism was proposed to explain either the high activity with planar, unhalogenated OEP, or the "activation" of the carbonyl porphyrins by acid.

In addition to catalysis observed with N-oxides and peroxides, the dioxo ruthenium porphyrins are a unique example of porphyrin catalysis with dioxygen but without addition of a coreductant. $Ru^{VI}TMP(O)_2$ catalyzes the aerobic oxidation of olefins under mild conditions.[11] The proposed mechanism (Figure 5.1) suggests that $Ru^{IV}TMP(O)$, formed upon a single oxidation of substrate, disproportionates to reform the active Ru^{VI} species and a solvated ruthenium(II) porphyrin, $Ru^{II}TMP(S)_2$.[12] The weakly coordinated ruthenium(II) reacts with O_2 to complete the cycle. While other porphyrins such as $Ru^{VI}OEP(O)_2$ and $Ru^{VI}TPP(O)_2$ share the ability to stoichiometrically oxidize alkenes, the less sterically bulky compounds dimerize to $(Ru^{IV}P(OH))_2O$ rather than reform $Ru^{VI}P(O)_2$ in the presence of dioxygen.[17,18]

RuTMP(O)$_2$ has been utilized as a catalyst for the aerobic oxidation of thioethers, steroids, and esters.[19-22] Although these papers describe catalysis by RuTMP(O)$_2$ in good yield, few experiments have been conducted to probe the validity of the initially proposed Groves mechanism (Figure 5.1). Furthermore, there has been little comment on the unusual ability to activate dioxygen in combination with the inability of this species to oxidize alkanes. The mechanism of RuP(CO) activation by strong acid, or the possibility of a different mechanism with N-oxides (versus dioxygen) have also not been adequately addressed. In summary, although some of the extremely interesting and unique chemistry displayed by ruthenium porphyrins has been noted, little of it is well understood.

Our investigations into oxidation catalysis with perhalogenated iron porphyrins (Chapter 4) led to the synthesis and characterization of a perhalogenated ruthenium porphyrin complex, β-octachloro-tetrakis(pentafluorophenyl)porphyrinato-ruthenium(II) carbonyl (RuTFPPCl$_8$(CO)) (Chapters 2 and 3). Initially, the ruthenium porphyrin was to be used to generate stable ruthenium analogs to iron peroxy intermediates proposed in the decomposition of alkyl peroxides by Fe(TFPPBr$_8$)Cl, allowing a better understanding of the iron oxidation mechanism. Alternatively, the halogenated porphyrin could share the unusual reactivity of Ru^{II}TMP with dioxygen. Catalytic activity in iron porphyrins has been shown to increase with the anodic shift in the iron reduction potential, suggesting that a halogenated ruthenium porphyrin may show higher activity than RuTMP. Indeed, RuTFPPCl$_8$(CO) is an extremely active catalyst for olefin oxidation with dioxygen. The mechanism does not appear to be related to either the other halogenated metalloporphyrins or the unhalogenated ruthenium porphyrins, but is unique to RuTFPPCl$_8$(CO).

Results

RuTFPPCl$_8$(CO) is an efficient catalyst for the oxidation of alkenes with PhIO or molecular oxygen. The oxidation reactions were run under comparable conditions to those with Fe(TFPPBr$_8$)Cl described in Chapter 4. Each reaction was initiated by addition of 1 mL substrate to 15 mL of a 0.1 mM solution of RuTFPPCl$_8$(CO) in methylene chloride. The reaction vessel (Figure 4.9) also contained 40 equivalents iodosobenzene under argon, or if O$_2$ was the oxygen source, the solution and head space in the reaction vessel were saturated with dioxygen. Aliquots were taken every 2 hours and products detected by GC.

Iodosobenzene is not a very efficient oxygen source for cyclohexene oxidation with RuTFPPCl$_8$(CO) (Figure 5.2, Table 5.1). Only 10 turnovers are observed in 24 hours, with formation of 42% epoxide. The selectivity for epoxide is less than with Fe(TFPPBr$_8$)Cl, but a notable lack of ketone is produced (< 2%). The reaction rate is highest initially, tapering off after the first 6 hours. The UV-Vis spectrum remains unchanged at the end of 24 hours, indicating that the decrease in rate is not due to porphyrin decomposition. Styrene is better oxidized by iodosobenzene and RuTFPPCl$_8$(CO), with 26 turnovers in only 3 hours, 81% of which are styrene oxide.

The high selectivity for epoxidation observed with PhIO and RuTFPPCl$_8$(CO) is consistent with formation of Ru^{IV}TFPPCl$_8$(O). As described in Chapter 4, iodosobenzene reacts with metalloporphyrins to form a metal-oxo intermediate. In the presence of olefin, the oxo species forms a charge transfer complex that may lead to epoxidation via concerted oxene transfer or electrophillic addition to the carbon-carbon double bond (Figure 4.3). The decreased activity for cyclohexene oxidation by Ru^{IV}TFPPCl$_8$(O) relative to "Fe^V(TFPPBr$_8$)Cl(O)" is not surprising, since the ruthenium porphyrin is one oxidation state lower than the iron analog.

Activity with dioxygen is quite substantial (Table 5.1). In 24 hours, 42 equivalents of cyclooctene are epoxidized to cyclooctene oxide. Benzaldehyde is the

sole product of styrene oxidation, producing only 2.5 turnovers in 3 hours. The greatest activity is seen in the oxidation of cyclohexene; 296 turnovers consisting of cyclohexene oxide (15%), 2-cyclohexen-1-ol (58%) and 2-cyclohexen-1-one (27%) are observed in 24 hours (Figure 5.3).

The mechanism with dioxygen is not as obvious. The different product selectivity observed in oxidation of both styrene and cyclohexene with dioxygen versus iodosobenzene suggests there is a different mechanism for the two O-atom sources. The increased amount of allylic and carbon-carbon bond cleavage oxidation products suggests that the mechanism with O_2 has a substantial radical contribution. Since reactions with PhIO are believed to go through a Ru^{IV} oxo intermediate, a different oxidizing species must be generated upon reaction with O_2. Unfortunately, the difficulty in obtaining large quantities of porphyrin has precluded the direct observation of intermediates in the dioxygen reactions. Instead, indirect methods have been used to probe the reaction mechanism. As many modes of interaction between oxygen and the porphyrin are possible, we have tried to test the viability of the most likely candidates.

A simple, direct method of dioxygen activation mimics dioxygenase rather than monooxygenase activity (Figure 4.7). Such a mechanism, initially proposed to explain oxidations with highly halogenated iron porphyrins,[23] is even more attractive for the ruthenium analogs, since no addition of coreductant would be required to initiate the cycle. Oxygen binds to $RuTFPPCl_8(CO)$, which reacts with another porphyrin molecule to form a μ-peroxo dimer, $(TFPPCl_8)Ru^{III}-O-O-Ru^{III}(TFPPCl_8)$. Homolytic O-O bond cleavage forms the active oxidant, Ru^{IV} monooxo, which returns to the catalyst resting state after oxidizing substrate. This mechanism is unlikely for two reasons. First, cleavage of the μ-peroxo bond to form $(P)Ru^{IV}=O$ would produce the same oxidizing species as PhIO, and would therefore be expected to yield the same product distribution. This mechanism does not allow for the different selectivity observed with different oxidants. Furthermore, $Ru^{II}TFPPCl_8(CO)$ is air stable and shows no reaction with

dioxygen, even upon recrystallization from an air saturated solution. Thus the first step in the cycle does not occur.

A second possibility is that $RuTFPPCl_8(CO)$ and $Fe(TFPPBr_8)Cl$ operate by the same mechanism with oxygen (Figure 4.8). A plot of moles of cyclohexene product versus time for catalysis by $RuTFPPCl_8(CO)$ (Figure 5.3) shows a slight curvature, suggesting some initiation for this catalyst, although not as significant as observed for the iron analog. More importantly, no metal couple is accessible in the ruthenium porphyrin electrochemistry (Chapter 3), so no orbital of reasonable energy is available to transfer electrons to or from an alkyl peroxide.

The best evidence that $RuTFPPCl_8(CO)$ does not operate by an alkyl peroxide decomposition mechanism, however, is that it does not decompose peroxides at an appreciable rate. $Fe(TFPPBr_8)Cl$ has been shown to rapidly decompose *tert*-butyl hydroperoxide[24,25]; when TBHP is added to a solution of $Fe(TFPPBr_8)Cl$, oxygen is vigorously evolved. A similar concentration of $RuTFPPCl_8(CO)$ does not exhibit a visible reaction. A more sensitive analysis of hydrogen peroxide decomposition shows that the ruthenium porphyrin only decomposes 4.5 equivalents of peroxide in four hours, as measured by oxygen evolution. The iron porphyrin is much more efficient, with 68 turnovers in the same time period (Figure 5.4). The opposite relative activity is observed for cyclohexene oxidation with dioxygen, where $RuTFPPCl_8(CO)$ catalyzes 296 turnovers compared to only 73 by $Fe(TFPPBr_8)Cl$ in 24 hours. A purely radical peroxide decomposition mechanism is not consistent with these observations.

A third possibility is that this catalyst mimics the behavior of RuTMP(CO) with oxygen. A Ru^{VI} dioxo complex would be expected to exhibit different reactivity than a monooxo, thus resolving the problem of dissimilarity with the iodosobenzene results. Therefore an attempt was made to reproduce the Groves cycle with $RuTFPPCl_8(CO)$. As in the conversion of RuTMP(CO) to $Ru^{VI}TMP(O)_2$,[10] careful titration of a solution of $RuTFPPCl_8(CO)$ with mCPBA resulted in complete formation of a new species

(λ_{max} = 420, 514, 552 nm) after addition of two equivalents peroxide (Figure 5.5).
Isosbestic points at 390, 417, 525, and 585 nm indicate that only a single species is
formed. The slight red shift in the Soret band and the blue shift in the Q bands are
consistent with spectral changes observed in the oxidation of RuOEP(CO) to
RuOEP(O)$_2$,[18] suggesting that Ru^{VI}TFPPCl$_8$(O)$_2$ is formed. The disappearance of the
carbonyl stretch in the IR indicates removal of the CO ligand, but no strong stretch is
observable in the 700 to 900 cm^{-1} region, as would be expected for a ruthenium oxo.[12,18]
However, this region contains strong solvent stretches, making detection of $\nu_{Ru=O}$
difficult by solution infrared spectroscopy.

The anodically shifted reduction potentials of RuTFPPCl$_8$(CO) would destabilize
the higher oxidation states relative to those of RuTPP complexes, making
Ru^{VI}TFPPCl$_8$(O)$_2$ extremely reactive. In line with this expectation, any attempt to
concentrate or isolate this species led to decomposition to a variety of porphyrin products.
However, at low concentrations, such as in a range where UV-Visible spectroscopy of the
porphyrin ligand is feasible (1 - 10 μM), the steps of the catalytic cycle can be observed
(Figure 5.6). Addition of mCPBA to form Ru^{VI}TFPPCl$_8$(O)$_2$, followed by addition of a
small amount of cyclohexene, results in a large decrease in the intensity of both the Soret
and Q band absorptions. The bleach is not due to porphyrin decomposition, because
addition of carbon monoxide gas regenerates the original spectrum with over 85% of the
original intensity. The new spectrum is similar to that of Ru^{IV}OEP(O)[26] or
Ru^{IV}TPP(O),[17] with a slight blue shift in the Soret band and broad absorptions in the Q
band region relative to the dioxo complex, suggesting formation of Ru^{IV}TFPPCl$_8$(O).
Increased recovery of the Soret band after 24 hours in the presence of substrate could
indicate transfer of the second oxo ligand from Ru^{IV}TFPPCl$_8$(O) to form another
molecule of oxidized substrate and Ru^{II}TFPPCl$_8$(S)$_2$. Unfortunately, the amount of
product generated was too small to be detected by the GC method used for the general
catalysis experiments, and oxo-transfer to the olefin could not be confirmed.[27]

Oxidation of triphenylphosphine to triphenylphosphine oxide can be confirmed by ^{31}P NMR. Addition of two equivalents PPh$_3$ to a solution of Ru^{VI}TFPPCl$_8$(O)$_2$ led to a decrease in the 514 nm band and the 600 nm tailing associated with dioxo formation, and new Q bands at 542 and 553 nm (Figure 5.7a). Continued addition of PPh$_3$ resulted in a blue shift of the Q bands to 517 and 540 nm, which may correspond to the coordination of triphenylphosphine to Ru^{II}TFPPCl$_8$ (Figure 5.7b). These two steps are believed to correspond to oxidation of 2 eq PPh$_3$ by the dioxo porphyrin followed by coordination of PPh$_3$ to the solvated ruthenium(II) porphyrin.

The ^{31}P NMR of this sample after the reaction is complete does show a resonance for Ph$_3$PO at 29.9 ppm. A second signal, consistent with PPh$_3$ coordination to Ru^{II}, appears at 40 ppm in the ^{31}P NMR (no signal is observed at -6 ppm for free triphenyl-phosphine). For example, Ru(COOMe)$_2$(CO)$_2$PPh$_3$ has a chemical shift of 30.5 ppm.[28] Although the UV-Vis showed isosbestic conversion to "RuTFPPCl$_8$(PPh$_3$)$_2$", the ^{19}F NMR was not clean, indicating that coordination of triphenylphosphine is not quantitative. Additional peaks in the ^{19}F NMR may be due to partial degradation of the porphyrin ligand after treatment with a harsh oxidant such as mCPBA.

Addition of styrene to a solution of Ru^{VI}TFPPCl$_8$(O)$_2$ led to similar spectroscopic changes, indicating that the decrease in Soret intensity ("oxo transfer") is not dependent on the substrate. In the absence of a potential ligand, the Soret bleach was even more pronounced. Addition of a small amount of pyridine to this solution led to the formation of RuTFPPCl$_8$(py)$_2$ (confirmed by UV-Vis). The ease of formation of the bis-pyridine adduct is consistent with oxidation of substrate by Ru^{VI}TFPPCl$_8$(O)$_2$ to form Ru^{II}TFPPCl$_8$(S)$_2$ that is able to coordinate an available ligand.

These experiments suggest that RuTFPPCl$_8$(CO) can undergo Groves type chemistry. The catalytic oxidation reactions with O$_2$, however, were conducted without any additional oxidant, allowing no mechanism for the initial formation of Ru^{VI}TFPPCl$_8$(O)$_2$ from the carbonyl species. In addition, oxo transfer is generally

accepted to be more selective than the catalysis observed in the dioxygen reactions. Although Groves chemistry is possible, it does not seem probable for the main mechanism for catalysis by RuTFPPCl$_8$(CO) with dioxygen.

Therefore a modified mechanism is proposed, which reacts through the lower oxidation states, involving both a monooxo and a peroxo intermediate. As mentioned above, Ru^{IV}TMP(O) is a weak oxo transfer agent; the more electron-withdrawing TFPPCl$_8$ ligand would be expected to result in a much more reactive monooxo complex. The reaction is initiated by a slow loss of CO (Figure 5.8). The solvated ruthenium(II) porphyrin, without the strong π acid effect of the carbonyl, would have a much lower Ru$^{III/II}$ couple, increasing the possibility of a reaction with dioxygen. Instead of forming Ru^{IV}TFPPCl$_8$(O), as in the direct oxygen activation mechanism (Figure 4.7), the ruthenium(II) dioxygen complex could rearrange to a ruthenium peroxo species that can react with substrate. The peroxide intermediate can either abstract a hydrogen atom from substrate to form Ru^{III}TFPPCl$_8$(OOH) or attack olefin to epoxidize one substrate molecule and form Ru^{IV}TFPPCl$_8$(O). The branching at this point in the mechanism would accommodate the observation of allylic oxidation products from escape of R$\bullet$ which could initiate a free radical reaction. Decomposition of the alkyl peroxide radical to product and RuTFPPCl$_8$(O) would result in a larger amount of epoxide formation relative to the purely radical alkyl peroxide mechanism of Fe(TFPPBr$_8$)Cl. This mechanism is similar to one proposed for stoichiometric oxidation by vanadium(V) peroxo complexes where a mixture of epoxidation and hydroxylation was observed.[29]

The modified peroxo intermediate mechanism does implicate an initiation period for the catalyst, as loss of the carbonyl ligand is required before interaction with dioxygen can occur. Chemical removal of the carbonyl ligand should abolish the initiation period and increase the amount of active catalyst, resulting in higher overall product formation. However, addition of a small amount of triethylamine-N-oxide (10 eq) or mCPBA (5-10 eq) to remove the carbonyl ligand did not increase the rate of reaction. The oxidation

reactions were initiated by addition of oxygen and cyclohexene to a solution of RuTFPPCl$_8$(CO) and (Et)$_3$NO or mCPBA. No change in the rate of catalysis was observed with triethylamine-N-oxide (Figure 5.9), though the product distribution was much more similar to that of Fe(TFPPBr$_8$)Cl with dioxygen, with only 6% epoxide and 59% 2-cyclohexen-1-ol. The porphyrin spectrum was also affected by addition of (Et)$_3$NO. The Q band absorptions grew in intensity and moved to 510 and 535 nm, similar to the spectrum of RuTFPPCl$_8$(py)$_2$, suggesting that triethylamine may bind to ruthenium.

Reactions with mCPBA were substantially different; only 20 turnovers were observed, all within the first 2 hours. More epoxide was produced: 35% versus 15% with dioxygen alone. The lack of products suggests that the catalyst deactivated, although the spectrum was unchanged. It is possible that Ru^{II}TFPPCl$_8$(L)$_2$ remaining after the reaction with mCPBA dimerizes or forms another porphyrin product with a Soret at similar energy to RuTFPPCl$_8$(CO). Although titrations with mCPBA suggest relatively stable formation of Ru^{VI}TFPPCl$_8$(O)$_2$, the catalysis experiments are run at significantly higher concentration of porphyrin (> 25 X). The lack of activity suggests that the carbonyl free porphyrin is not stable at higher concentrations, and perhaps dimerizes to a catalytically inactive species. In a normal cyclohexene oxidation reaction, only a small amount of ruthenium porphyrin is an active catalyst (has lost CO) at any given time. Therefore the concentration of Ru^{IV}TFPPCl$_8$(O) is quite low, and reacts with substrate before deactivation (via dimerization) can occur. Alternatively, the mechanism proposed in Figure 5.9 may be incorrect; the carbonyl ligand may remain on the ruthenium for the duration of the reaction, and activation of the catalyst occurs by some other means.

Addition of TBHP could also serve to initiate the reaction. Unlike mCPBA, TBHP is not a strong enough oxidant to remove the carbonyl ligand. However, it is capable of generating free radicals, and could initiate a radical based reaction in solution.

Addition of 10 equivalents TBHP to a solution of RuTFPPCl$_8$(CO) in the presence of cyclohexene and O$_2$ results in no increase in the number of moles of products produced (Figure 5.10a). The product distribution in these reactions is the same as with dioxygen alone.

If a larger amount of TBHP is added, the reaction is much faster, with 200 turnovers in the first hour. The product distribution is also significantly different, with 10% epoxide and 50% 2-cyclohexen-1-ol throughout the run. It is not clear if the porphyrin is involved in this chemistry, or if the TBHP has simply initiated a free radical reaction. If the data is replotted in terms of turnovers, then a significant increase in rate is observed with either 10 or 300 equivalents of TBHP (Figure 5.10b). Interpretation of this result is complicated by the fact that only 50% as much porphyrin catalyst was used in the peroxide experiment.

Phase transfer of dioxygen into the solution is not rate limiting. Although solubility of dioxygen in methylene chloride is only 10 mM, this does not limit the reaction rate. A decrease in the stir rate (Figure 5.11) or even a complete lack of stirring does not curtail the rate of product formation. In fact, as seen in Figure 5.11, the slower stirred reaction showed more turnovers in an equal time period. A completely unstirred reaction also showed slightly higher activity, suggesting that a lower concentration of oxygen in solution may enhance reactivity.

A further test of the peroxo mechanism used the presence of additional carbon monoxide to inhibit the reaction. If catalyst activation involves spontaneous loss of CO, exposure to a carbon monoxide atmosphere should shut down catalysis by pushing the equilibrium towards the inactive CO bound form. As mentioned above, both UV-Vis and IR spectroscopy indicate that the carbonyl ligand remains bound both during and after a catalytic run. However, the presence of a small amount of ruthenium porphyrin without CO would be difficult to detect by these methods. To further explore the role of the carbonyl ligand, oxidation of cyclohexene by RuTFPPCl$_8$(CO) was conducted under a

mixture of oxygen and carbon monoxide. Rather than preventing oxidation, identical rates of product formation were observed under a 50/50 O_2/CO atmosphere. The mixed atmosphere reaction only produced less product at the 24 hour time point, since only half as much total oxygen was in the reaction vessel (Figure 5.12).

The lack of inhibition by CO, while not encouraging, does not completely rule out the loss of CO as the first step in the reaction mechanism. As described above, if the carbonyl ligand is never lost, the subsequent reaction with dioxygen would never occur. However, if the reaction with dioxygen is much faster than recombination with carbon monoxide, some ruthenium porphyrin would remain active, allowing oxidation chemistry to take place in the presence of CO. However, it is surprising that absolutely no decrease in rate is observed.

A more interesting result from the mixed atmosphere experiments is the decrease in epoxide formation. At 24 hours, epoxide comprises only 7% of the total products, compared to 15% in a pure dioxygen environment. The decrease in epoxidation is offset by an increase in the amount of 2-cyclohexen-1-one to 36%. A possible explanation for the change in product distribution is that multiple oxidation pathways with dioxygen are available, and one that favors epoxidation is inhibited by carbon monoxide, while the other is not.

To insure that a small amount of uncarbonylated porphyrin is not present, a sample was exposed to a high pressure of CO. A small amount of RuTFPPCl$_8$(CO) in CCl$_4$ or CH$_2$Cl$_2$ was placed into a Parr reactor and sealed under 1100 psi of carbon monoxide for 2 or 4 days. The pressure was released from the Parr bomb, and a measured amount of the porphyrin solution (containing ~ 2 μmol porphyrin) was injected directly into a solution of methylene chloride and cyclohexene to initiate a dioxygen catalysis reaction. Some carbon monoxide remained in the porphyrin solution, but as the mixed atmosphere experiments demonstrated, the presence of a small amount of CO does not inhibit the oxidation reaction.

Catalysis with the CO treated RuTFPPCl$_8$(CO), however, had an extremely long initiation period. In 24 hours, only ten turnovers are observed, composed entirely of allylic oxidation products. By 48 hours, the reaction has fully initiated, with 238 turnovers comprised of 7% epoxide, 53% 2-cyclohexen-1-ol, and 40% 2-cyclohexen-one, similar to the product distribution observed in the mixed atmosphere reactions.

Spectroscopy of the CO treated porphyrin showed that the porphyrin had been modified during the long exposure to CO. The infrared spectrum of the porphyrin shows a new peak at 2112 cm^{-1} in addition to the peak assigned to the CO stretch of mono-carbonyl complex at 1981 cm^{-1}. The shift of v_{CO} to higher energy is consistent with formation of RuTFPPCl$_8$(CO)$_2$; calculations indicate that a single CO stretch is expected for the bis-carbonyl porphyrin (approximating the porphyrin as D_{2d} symmetry). An intense peak also appeared in the IR spectrum at 1730 cm^{-1}, as discussed below.

The UV-Vis spectrum in either methylene chloride or carbon tetrachloride showed a slight red shift of the Soret to 420 nm and a slight blue shift and broadening of the Q bands (Figure 5.13). A strong absorption was also observed at 280 nm, but is not believed to be related to the porphyrin, since it appeared at different intensity relative to the porphyrin bands in the two runs. The high energy electronic transition and the 1730 cm^{-1} IR band are consistent with signals from a ketone. It is possible that some reaction between the reactive halogenated solvent and carbon monoxide could have occurred, resulting in formation of an acyl chloride or halogenated ketone. Low molecular weight acyl chlorides have a strong absorption around 1800 cm^{-1}, while halogenated ketones are at slightly lower energy. ^{1}H NMR of the carbon tetrachloride solution after removal from the Parr reactor showed a weak resonance at 4.3 ppm; chloroacetyl chloride has a chemical shift of 4.6 ppm. Unfortunately, it is impossible to do more than speculate on the source of these organic-type absorptions. However, repurification of the porphyrin by column chromotography does remove the 280 nm band from the UV-Vis and the 2112 cm^{-1} band from the IR. The purified porphyrin regains

catalytic activity, suggesting that chromotography removes the second CO from the ruthenium. In the absence of another axial ligand to displace the second carbonyl, such as water or acetone available in the usual post-synthesis workup, the second carbonyl ligand remains bound. The bis-carbonyl complex has no coordination sites available for chemistry, and no catalysis is observed. The pressure experiments suggest some interesting activation of CO under high pressures, but do not elucidate the role of the carbonyl ligand in catalysis.

Oxidation reactions with cyclohexene-d_{10} show a large isotope effect in reactions with dioxygen (Figure 5.14). In competitive experiments with equal amounts of deuterated and non-deuterated cyclohexene, the ratio of products at 24 hours gives an isotope effect of 7.0. The product distribution indicates a significant difference between epoxidation and allylic oxidation. Epoxide formation has no isotope effect (ratio = 1.0), 2-cyclohexen-1-ol has an isotope effect of 14.1, and the isotope effect for 2-cyclohexen-1-one formation is twice that number (29.5), suggesting that different processes are responsible for epoxidation and hydroxylation. Both the total isotope effect (8.2) and the individual isotope effects (1.15 for epoxidation, 9.2 and 19.3 for allylic oxidation) are of similar magnitude to those of Fe(TFPPBr$_8$)Cl, suggesting that hydrogen abstraction is involved in the rate determining step.

Non-competitive experiments reveal that the two cases are not the same. With Fe(TFPPBr$_8$)Cl, no reaction was seen with cyclohexene-d_{10} alone. Presumably, spontaneous radical formation from deuterated cyclohexene is slow due to the stronger C-D bond, and the reaction is never initiated. With RuTFPPCl$_8$(CO), however, some reaction with cyclohexene-d_{10} was observed, indicating that the ruthenium porphyrin does not initiate solely by the same mechanism as the iron porphyrin. The non-competitive isotope effect is extremely large, (mol cyclohexene products)/(mol cyclohexene-d_{10} products) = 85. A large non-competitive isotope effect (50) has been reported for the oxidation of alcohols by [(bpy)$_2$(py)Ru^{IV}(O)]$^{2+}$.[30] The mechanism

involves hydride transfer followed by rapid proton equilibration from the aqueous medium, which is not applicable to the organic solvent reaction of RuTFPPCl$_8$(CO).

Further experiments probed the possibility of a photochemical reaction. Since the reaction vessel is made of glass, ambient light enters the reaction, allowing the possibility of a light activated mechanism. Porphyrins are known to sensitize singlet oxygen,[31] and the actual oxygen transfer step could be completely unrelated to the ruthenium center. To test the possibility of singlet oxygen production, ZnTFPPCl$_8$ was used in place of RuTFPPCl$_8$(CO). Visible light has enough energy to cause a $\pi \rightarrow \pi^*$ transition in either the zinc or ruthenium porphyrin to form a triplet excited state. The triplet can act as a sensitizer to generate singlet oxygen, which could then react with cyclohexene. Under similar conditions to catalysis with RuTFPPCl$_8$(CO), ZnTFPPCl$_8$ produced only 3 turnovers of cyclohexene in 24 hours, all of which were allylic oxidation products. This is within the range of products observed without any catalyst (between zero and 20 µmol product, approximately equal to up to 10 turnovers), suggesting that ZnTFPPCl$_8$ does not catalyze the oxidation of cyclohexene by any mechanism. The lack of activity from the porphyrin suggests that the TFPPCl$_8$ ligand is not an efficient oxygen sensitizer. Furthermore, the products are not consistent with an organic singlet oxygen reaction. $^1O_2$ generates ketones and carbon - carbon bond cleavage products rather than epoxides and alcohols.[32]

A second control was performed by excluding light from a catalysis reaction of RuTFPPCl$_8$(CO) with dioxygen and cyclohexene. The initiation period increased dramatically, with almost no reaction in the first 10 hours. The initiation period for one reaction was longer than the second trial, resulting in very different turnover numbers at 24 hours (Figure 5.15). Once started, however, the reaction rate does increase; at 24 hours, Run 1 has 75% of the products of an average reaction in ambient light. The second reaction, which was slower to initiate, has only 16% as much activity in 24 hours. Product distributions are similar to a reaction in the light, suggesting that the same

mechanism is operating in both cases. Although singlet oxygen is not implicated, ambient light does play a role in initiating the reaction with $RuTFPPCl_8(CO)$ and O_2. The catalyst appears to be both thermally and photochemically activated.

Photolysis with visible light dramatically increases the rate of reaction (Figure 5.16). Two identical reactions were set up, one in the presence of normal room light (one light bulb from a hood lamp), and one continuously irradiated with a tungsten lamp (150W). The visible photolysis reaction shows 3.5 times as many turnovers in 8 hours (270 vs. 77), a tremendous enhancement by relatively low energy light. No porphyrin decomposition was observed. Product distributions are similar in the two reactions, indicating that a similar reaction is occurring in both cases.

To further explore the effect of light, the photophysics of $RuTFPPCl_8(CO)$ were investigated. Samples of $RuTFPPCl_8(CO)$ in methylene chloride were irradiated with pulses from a Nd-YAG or dye laser. Laser photolysis is known to photodissociate carbonyl ligands,[8] allowing an investigation of the reactivity of the bare ruthenium porphyrin. Excitation with 355 or 480 nm light produced a transient difference spectrum consistent with promotion of an electron into the π^* e_g orbital. A positive absorbance at 620 nm (Figure 5.17) and a negative change in optical density (ΔOD) in the Soret region indicate formation of a porphyrin triplet.

The kinetics describing decay of the excited state were dependent on the atmosphere over the solution. Both the 5 μs and 50 μs transient absorption spectra from 390 to 440 nm were obtained under carbon monoxide, ethylene, oxygen, and argon atmospheres; the transient spectra at 415 nm are shown in Figures 5.18 and 5.19 (additional traces are in Appendix 5). Under CO, biexponential decay of the excited state is observed. The faster rate,[33] $k_1 = 3.9 \times 10^6 \, s^{-1}$, most likely corresponds to the decay of the porphyrin triplet excited state. The lifetime, 286 ns, is much shorter than the 36 μs porphyrin-based triplet excited state of $RuTPP(CO)$,[34] but longer than the 15 ns charge transfer excited state of $RuTPP(py)_2$.[35] Generally, ruthenium porphyrin complexes have

$^3(\pi - \pi^*)$ lifetimes of tens of microseconds, while $(d - \pi^*)$ lifetimes are only a few nanoseconds.[31] Although the transient spectrum (at t = 0; Figure 5.17) shows porphyrin triplet characteristics, the short lifetime suggests that substantial mixing of the triplet and charge transfer states is occurring. The molecular orbital diagram of $RuTFPPCl_8(CO)$ (Figure 3.6) indicates that these two transitions are expected to be very close in energy. No emission was detected either at room temperature or from 2-methyl-tetrahydrofuran glass (77 K) at any wavelength out to 1100 nm.

The second kinetic term, $k_2 = 1.3 \times 10^5\,s^{-1}$, is believed to be due to recombination of CO. The concentration of CO in chloroform is 8.5 mM; assuming pseudo first order kinetics (and a similar concentration in CH_2Cl_2), the CO recombination rate is calculated as $1.5 \times 10^7\,M^{-1}\,s^{-1}$.

As observed in the laser traces at 415 nm on a 50 μs time base (Figure 5.19), the signal does not completely return to zero. The transient at 50 μs is after the excited state has decayed, and should correspond to the spectrum of the photoproduct from loss of the carbonyl ligand. The magnitude of the ΔOD indicates that the quantum yield for loss of CO is quite small, consistent with quantum yields observed for other ruthenium porphyrins.[8] Comparisons of the transient spectra under different atmospheres at 50 μs may give some indication of the reactivity of the carbonyl free ruthenium.

Oxygen efficiently quenches the triplet at a rate of $1.25 \times 10^7\,s^{-1}$. However, comparison of the transient absorption spectra at 50 μs under CO and O_2 does not suggest that oxygen binds to ruthenium (Figure 5.20). In fact, none of the spectra from the four samples have a distinct photoproduct at 50 μs, not supporting a mechanism involving oxygen binding to $RuTFPPCl_8$ after loss of CO. Furthermore, a spectrum taken of each sample after laser photolysis (Figure 5.21) indicates that significant amounts of porphyrin decomposition occur under an oxygen atmosphere.

An ethylene atmosphere results in decay rates of $k_1 = 8.9 \times 10^6\,s^{-1}$ and $k_2 = 4.2 \times 10^5\,s^{-1}$, indicating substantial quenching of the porphyrin excited state. Since ethylene is

unable to quench an excited state by energy transfer, it must be interacting more directly with the porphyrin to protect it from decomposition. The 50 μs transient under ethylene shows the greatest bleach in the Soret region, suggesting some interaction between ruthenium and olefin on this time scale. The ethylene sample shows no decomposition after photolysis, and even shows a slight increase in the Soret intensity. One explanation for these results is that ethylene binds to the excited state of $RuTFPPCl_8(CO)$ (k_1), and also to the photodissociated ruthenium porphyrin (k_2). Approximating the concentration of ethylene in solution as 5 mM gives an ethylene recombination rate with the photodissociated $RuTFPPCl_8$ of $8.4 \times 10^7 \, M^{-1} \, s^{-1}$. However, olefin complexation after loss of CO is not likely to be relevant to the catalytic mechanism since the quantum yield is very small. Photolysis of CO is only observed with high energy light (355 nm), and the oxidation reactions are only irradiated with visible wavelengths.

Under an atmosphere of argon, the excited state again shows biexponential decay kinetics with $k_1 = 7.1 \times 10^6 \, s^{-1}$ and $k_2 = 7.6 \times 10^5 \, s^{-1}$. These results are not consistent with the description of the ethylene and dioxygen chemistry above. It is difficult to find an explanation for the increase in the decay rates under an inert atmosphere. One possibility is that the in the absence of another ligand, the excited state interacts with methylene chloride, which is not a completely inert solvent. However, the decay rate would still be expected to be slower than rates under a CO atmosphere. A second possibility is that with the high energy light needed to observe the Soret band transients, multiple reactions may occur, complicating the kinetics.

Despite these problems, it is clear that excitation under ethylene results in a different product than photolysis under an inert atmosphere. Furthermore, although oxygen quenches the triplet excited state, there is no evidence for the substantial red shift normally observed upon binding of dioxygen.[4] These experiments suggest another possible mechanism that would initiate not with oxygen binding but with olefin binding. $RuTFPPCl_8(CO)$ is not able to catalyze the hydroxylation of alkanes with dioxygen,

suggesting that the electron richness of the carbon - carbon double bond is somehow important. Toluene, which has weak methyl C-H bonds, is not oxidized, either alone or in the presence of olefin to initiate reaction. Cumene or 3-methyl pentane, which is oxidized in low yield by Fe(TFPPBr$_8$)Cl, is also inactive with the ruthenium porphyrin and dioxygen.

Some evidence for olefin binding does exist. The carbonyl stretch in the solution IR of RuTFPPCl$_8$(CO) in CCl$_4$ shifts 2.2 cm^{-1} upon addition of a small amount of cyclohexene. The shift to higher energy is consistent with weak competition by the π * orbitals of the olefin for backbonding density from the ruthenium ion.

^{1}H NMR of RuTFPPCl$_8$(CO) in acetone-d_6 after 24 hours under an ethylene atmosphere showed a weak resonance at -3.6 ppm. RuTMP(C$_2$H$_4$) has a singlet at -3.27 ppm, assigned to a π complex of ethylene,[36] suggesting a similar assignment for RuTFPPCl$_8$(C$_2$H$_4$). The carbonyl ligand may remain bound to trans to the olefin, but it is not clear from the NMR data. As the signal is present under an atmosphere of ethylene gas, exchange of the bound ethylene must be slow on the NMR time scale. The ^{19}F NMR of this sample still showed several different porphyrin species, indicating that only a small fraction of the porphyrin has ethylene bound.

UV-Vis data indicates that olefin binding, if occurring, is not highly favored. A solution of RuTFPPCl$_8$(CO) with cyclohexene showed no change after 24 hours, suggesting that any olefin complex is of low enough concentration to be swamped by the signal of the carbonyl porphyrin. Alternatively, a weak interaction with olefin might cause only small changes in the UV-Vis spectrum.

If olefin binding is not favored for the ground state, the transient spectroscopy suggests that olefin binding may be more favorable in the excited state. A mechanism for catalytic olefin oxidation via the excited state is shown in Figure 5.22. The mixing of the $^3(\pi - \pi^*)$ and $(d - \pi^*)$ orbitals indicate that visible excitation of RuTFPPCl$_8$(CO) might populate the MLCT state which results in an oxidized metal center in the excited state.

Olefin binding to the strongly oxidizing Ru^{III} would then be more likely to occur (Figure 5.22). Once a π olefin complex is formed, it may rearrange to form a ruthenium(IV) alkyl radical complex, which would readily combine with dioxygen. The bound alkyl peroxide radical could abstract a hydrogen atom from another substrate molecule, forming a peroxide complex. From this point, several different pathways could occur. The peroxide could homolytically cleave, either thermally or photochemically, initiating a free radical reaction (not shown). Alternatively, the peroxide could decompose via an intermolecular epoxidation reaction, leaving $Ru^{III}TFPPCl_8(OH)$ (after the formal π radical anion recombines with the ruthenium), which may recombine with another radical, $R\cdot$, to form ROH and return the porphyrin to the resting state of the catalytic cycle.

This mechanism has several advantages over the mechanism involving loss of CO. First, spontaneous loss of the π acid carbonyl ligand is not likely for such an electron deficient porphyrin. Second, a partial carbon monoxide mechanism would not inhibit a photochemical reaction. Third, the dramatic increase in reactivity with light is explained by a greater amount of olefin complexation, which decomposes to lead directly to product or free radicals. The branching for a radical mechanism explains the large amount of allylic radical products observed. In addition, the large non-competitive isotope effect suggests that branching for the intermolecular mechanism is favored over C-D bond cleavage by a substantial amount, as is the high percentage of epoxidation formed with cyclohexene-d_{10}.

The peroxide experiments are also consistent with this mechanism. Addition of mCPBA removes the carbonyl ligand, which leads to a less oxidizing MLCT state with less or no affinity for olefin interaction. Addition of small amounts of TBHP may enhance the branching to the radical pathway by providing radicals to propagate radical reactions.

Conclusion

> Traditional scientific method has always been at the very best, 20-20
> hindsight. It's good for seeing where you've been. It's good for testing
> the truth of what you think you know, but it can't tell you where you
> ought to go.
>
> -- Robert M. Pirsig, *Zen and the Art of Motorcycle Maintenance*,
>   (1974).[37]

RuTFPPCl$_8$(CO) has unprecedented ability for a carbonyl porphyrin to catalyze the oxidation of olefins with dioxygen. The mechanism does not appear to be radical decomposition of alkyl peroxides, as observed with Fe(TFPPBr$_8$)Cl, or the Groves dioxo ruthenium(VI) chemistry observed with RuTMP. Instead, a novel mechanism is proposed that involves an interaction of olefin with a mixed $^3(\pi - \pi^*) - (d - \pi^*)$ excited state. The electron-withdrawing porphyrin ligand creates a highly oxidizing excited state ruthenium center, which can be stabilized by an interaction with a π donor ligand. Photochemically driven oxidation chemistry with such low energy, low intensity light is quite amazing.

The involvement of light in the mechanism is indisputable. The dramatic enhancement of catalysis by even low-energy irradiation clearly favors a photochemical reaction mechanism. This is unprecedented for this class of porphyrin catalysts. RuTFPPCl$_8$(CO) is unique in being the first stable, effective photocatalyst for olefin oxidation with dioxygen. Moreover, the catalyst would be extremely interesting for potential commercial applications since it fulfills the desired requirements of intense, low-energy light absorption.

Once olefin binding has occurred, the following steps in the reaction mechanism are not as clear. Although a logical mechanism can be proposed, further work would be necessary to completely understand the decomposition of the bound olefin/oxygen complex to form product. The potential also exists to tune the mechanism to favor one

branches of the proposed mechanism over another to increase the selectivity for epoxidation over hydroxylation. For example, selective photolysis at 420 nm (into the Soret band) could decrease undesired radical side reactions (such as decomposition of the bound alkylperoxide). Other conditions, such as solvent, temperature, and oxygen concentration have obvious potential to change the reaction selectivity. Since phase transfer is not rate limiting, perhaps a lower concentration of oxygen would increase the activity by decreasing unfavorable quenching of the excited state by oxygen (as suggested by the higher activity in the unstirred reactions).

A continuation of this project would include a more thorough investigation of the proposed photochemical activation of olefin. The photophysics of $RuTFPPCl_8(CO)$ could be better understood, especially the fast excited state decay under an argon atmosphere. Furthermore, if ethylene is quenching the $^3(\pi - \pi^*)$ excited state, varying the concentration of olefin would allow the quenching rate to be determined by Stern-Volmer kinetics. The possibility of a reaction with solvent could also be eliminated by repeating the reaction in a more inert solvent.

Experimental

Materials -- Ruthenium porphyrins were obtained as described in Chapter 2. Iodosobenzene and cyclohexene-d_{10} was purchased from TCI. Cyclohexene, cyclooctene (Aldrich), and methylene chloride (EM Science) were distilled under argon before use. Cyclohexene oxide, 2-cyclohexen-1-ol, 2-cyclohexen-1-one, m-chloroperoxybenzoic acid (mCPBA), *tert*-butyl hydroperoxide (TBHP), triethylamine-N-oxide, pyridine, and styrene were purchased from Aldrich. Hydrogen peroxide and acetone were purchased from EM Science. Carbon monoxide, ethylene, and dioxygen lecture bottles were purchased from Matheson.

Methods -- General oxidation reactions were conducted as described in Chapter 4. UV-Vis, NMR, and IR spectra were obtained as described in Chapters 2 and 3.

Reaction with peroxide -- Reactivity with TBHP was only determined in a qualitative fashion. Approximately 0.2 mL TBHP was added to a mM solution of either RuTFPPCl$_8$(CO) or Fe(TFPPBr$_8$)Cl in methylene chloride and allowed to stir for several hours. During this time, the solution was monitored visually for the evolution of gas that would indicate peroxide decomposition. A similar reaction with hydrogen peroxide was also monitored. In this case, 10 mg of porphyrin in 10 mL acetone was degassed on a high vacuum line. Five mL of 0.6 % hydrogen peroxide in acetone (degassed) was added, and the solution allowed to stir at room temperature. Every hour, the pressure of evolved gas was measured with a Toeppler pump and the number of moles calculated. An IR of the gas indicated that it was not carbon dioxide or carbon monoxide (from the carbonyl ligand of the ruthenium porphyrin), and was assumed to be dioxygen from the recombination of radicals produced from peroxide decomposition by the porphyrin.

Titration with mCPBA -- A solution of RuTFPPCl$_8$(CO) in methylene chloride, such that the absorbance at either the Soret or Q band was close to 1, was prepared and

the exact concentration determined by either serial dilution or from the extinction coefficient. A solution of mCPBA (mM) was prepared by serial dilution. The porphyrin solution (2.5 mL) was titrated with 10 to 20 μL aliquots of mCPBA, and monitored by UV-Vis. The changes in the spectrum were complete after addition of less than 100 μL mCPBA solution, such that the porphyrin concentration remained relatively constant.

Titration with triphenylphosphine -- Aliquots from a mM solution of PPh_3 were added to the porphyrin solution immediately after addition of mCPBA, and monitored by UV-Vis. The solution was concentrated and spiked with $CDCl_3$ for NMR analysis.

Initiation with mCPBA or $(Et)_3NO$ -- Five to ten equivalents of oxidant (approximately 1-3 mg) were added with the porphyrin to the reaction flask. Under argon, 15 mL of methylene chloride were added, and the solution allowed to stir for two minutes. The reaction vessel was flushed with dioxygen as 1 mL of cyclohexene was added to start the oxidation reaction. Product formation was measured as before.

Mixed atmosphere reactions -- $RuTFPPCl_8(CO)$, solvent, and cyclohexene were mixed together in the reaction flask under argon. A mixture of carbon monoxide and oxygen was used to flush the argon from the flask and start the oxidation reaction.

Pressurized carbon monoxide reaction -- A mM solution of $RuTFPPCl_8(CO)$ in either methylene chloride or carbon tetrachloride was placed in a glass lined Parr reactor. The reactor was connected to a carbon monoxide tank, and flushed twice before full pressurization to 1100 psi of CO. The reaction was not stirred, but allowed to rest under CO pressure for 2 or 4 days (in CCl_4 or CH_2Cl_2, respectively). The pressure was let down, the Parr reactor opened and the porphyrin solution transferred to a Teflon capped vial. One mL of solution was used to run an oxidation reaction by injecting it into the reaction just before addition of dioxygen and substrate. The concentration of $RuTFPPCl_8(CO)$ in the reaction was calculated from the absorbance of the porphyrin solution.

Initiate with TBHP -- Attempts to initiate cyclohexene oxidation reactions with peroxide were accomplished by addition of TBHP to the reaction before addition of substrate. A small amount of a dilute TBHP solution was added to a solution of RuTFPPCl$_8$(CO) in methylene chloride. Three separate reactions were run, adding 10, 225, or 380 equivalents of TBHP, respectively.

Stir rate -- The stir rate was lowered to half of normal for these reactions. One reaction was also run without any stirring.

Isotope effect -- The isotope effect was calculated from both competitive and non-competitive experiments. Competitive experiments were run with 15 mL of methylene chloride, 2 mg RuTFPPCl$_8$(CO), and 1 mL each of cyclohexene and cyclohexene-d_{10}. The deuterated oxidation products ran slightly slower on the GC, allowing individual determination of deuterated and non-deuterated turnover numbers. Non-competitive experiments were run with 1 mL of cyclohexene-d_{10}, and compared to reactions run with perprotio cyclohexene. The isotope effect was calculated as a ratio of turnover numbers at 24 hours, since actual rates of product formation were not determined from these experiments.

Singlet oxygen generation -- A cyclohexene oxidation reaction was run as described above, with 3 μmol ZnTFPPCl$_8$ in place of RuTFPPCl$_8$(CO).

Light experiments -- A cyclohexene oxidation reaction was run as described above, except the entire reaction flask was wrapped in foil to prevent incidental light from affecting the reaction. The light catalyzed reaction was accomplished by photolysis of an oxidation reaction with a normal 150 watt light bulb. The light was turned on before addition of substrate, and kept on for the duration of the experiment. The reaction was placed in a water bath to maintain ambient temperature.

Laser experiments -- Solutions of RuTFPPCl$_8$(CO) in methylene chloride were degassed by three cycles of the freeze/pump/thaw method on a high vacuum line in a quartz laser cuvette. The cuvettes were then backfilled with the desired gas (argon,
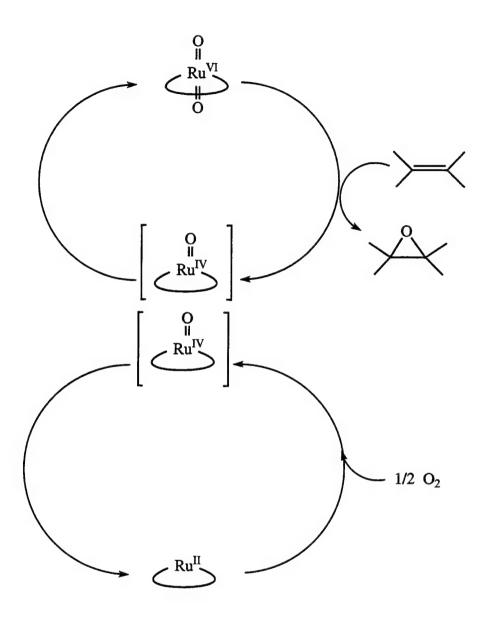
carbon monoxide, oxygen, or ethylene) to 1 atm pressure. The excitation source for the time resolved absorption experiments was the third harmonic of a Quanta-Ray Nd-YAG laser with a 20 nm pulse width; a PTi arc lamp supplied the white probe light source, and a DH 10 SA Inc. monochrometer was placed before the R955 Hamamatsu PMT detector. The analog signal was analyzed by a RTD 710A digitizer, and worked up on a 386 PC. The arc lamp power was 68 W, and in the case of weak signals the arc lamp was pulsed at 6 Hz. The signal was amplified with a fast amplifier designed at Brookhaven National Laboratories.[38] Further data manipulation was accomplished on either a 486 PC or a Macintosh IISi with computer programs written at Caltech.

References and Notes

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Figure 5.1 -- The Groves mechanism for catalytic oxidation of olefins with dioxygen by

$Ru^{VI}TMP(O)_2$. The ruthenium(IV) monooxo porphyrin disproportionates

to reform the active ruthenium(VI) catalyst (see reference 11).

$$Ru^{II} = \text{Ruthenium tetramesitylporphyrin}$$

Figure 5.2 -- Turnovers of cyclohexene by RuTFPPCl$_8$(CO) with iodosobenzene in 24 hours, showing the observed product distribution. Only 25% of the available oxidant is used.
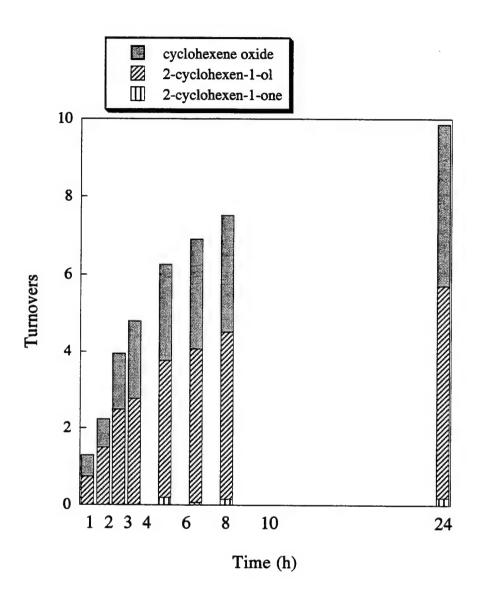
Figure 5.3 -- Turnovers of cyclohexene by RuTFPPCl$_8$(CO) with dioxygen in 24 hours, showing the observed product distribution. More allylic oxidation products are observed than with PhIO as the oxidant.
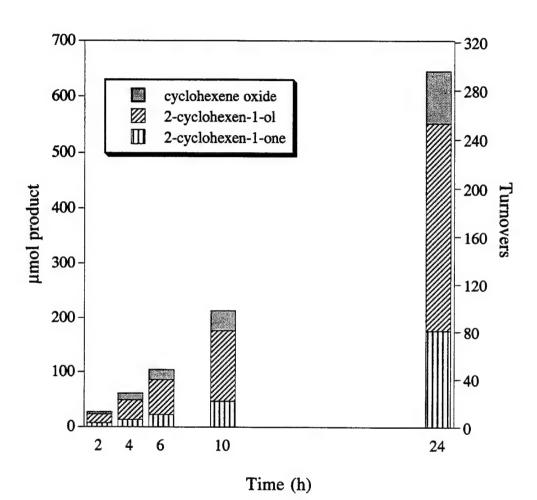
Figure 5.4 -- Hydrogen peroxide decomposition by $RuTFPPCl_8(CO)$ and $Fe(TFPPBr_8)Cl$
in acetone, as determined by oxygen evolution. The iron porphyrin
decomposes 68 turnovers in 4 hours, while the ruthenium porphyrin shows
much less activity in the same time period (4.5 TO).
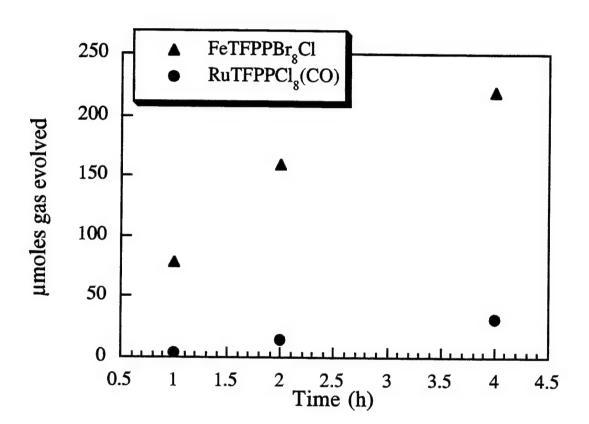
Figure 5.5 -- UV-Vis spectrum of RuTFPPCl$_8$(CO) upon titration with 2 equivalents of
mCPBA to form Ru^{VI}TFPPCl$_8$(O)$_2$. The red shift of the Soret band to
420 nm is consistent with dioxo formation.
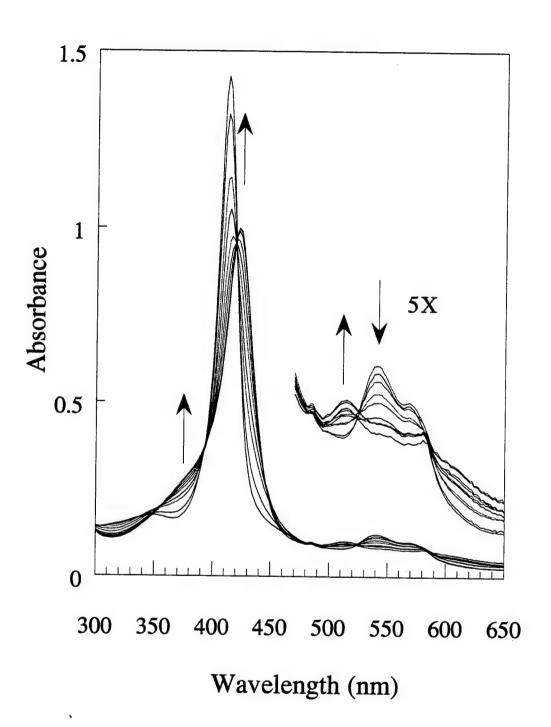
Figure 5.6 -- Addition of cyclohexene to Ru^{VI}TFPPCl$_8$(O)$_2$. The initial decrease in

Soret intensity corresponds to a single oxidation of substrate and

formation of Ru^{IV}TFPPCl$_8$(O). Eventually, the second oxo also transfers,

and addition of carbon monoxide gas regenerates the original spectrum of

Ru^{II}TFPPCl$_8$(CO) with 85% of the original intensity.
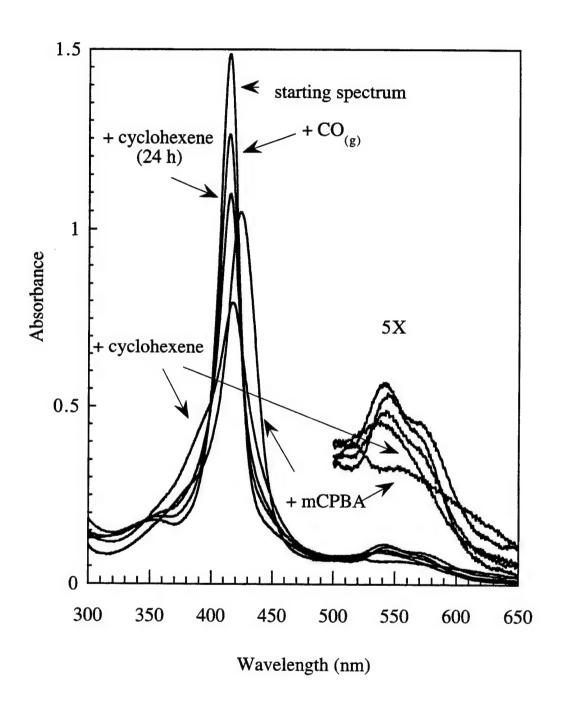
Figure 5.7 -- Addition of triphenylphosphine to $Ru^{VI}TFPPCl_8(O)_2$. The first 2 eq (a) are
believed to correspond to transfer of both oxo ligands. Further addition of
PPh_3 (2 eq, spectrum b) results in new spectral features consistent with
coordination of triphenylphosphine to the ruthenium porphyrin.

a) + 2 eq PPh₃

b) + 4 eq PPh₃ (total)
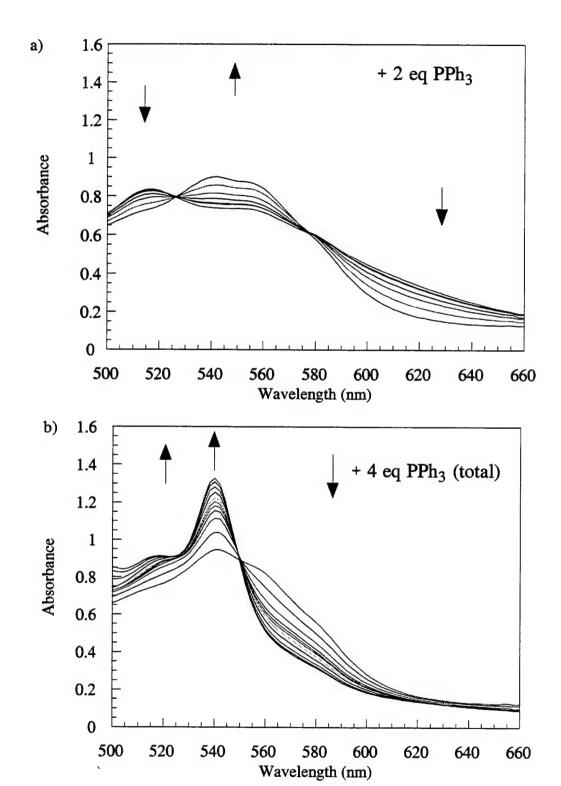
Figure 5.8 -- A potential mechanism for oxidation of olefins by $Ru^{II}TFPPCl_8(CO)$.

Initial loss of CO allows oxygen to bind to the electron poor metal center,

initiating the chemistry.

Ru^{III}OOH + R•

Free radical propagation <u>OR</u>
rebound to Ru^{IV}(O) and ROH
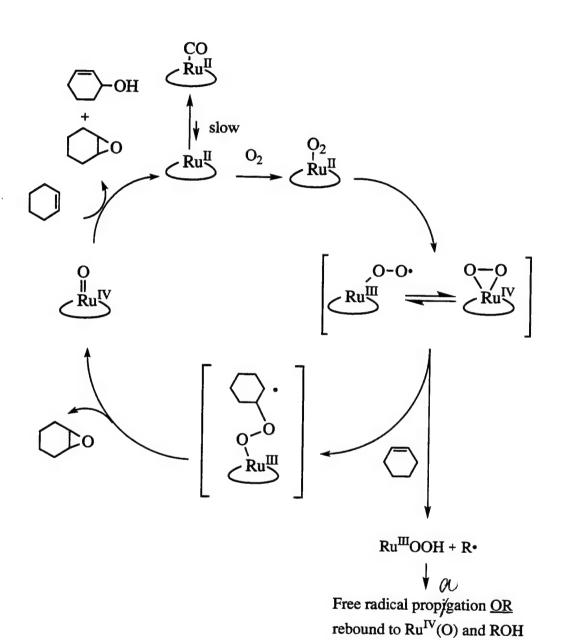
Figure 5.9 -- Relative rates of reaction for RuTFPPCl$_8$(CO) with dioxygen (a "normal" reaction) or in the presence of small amounts of (Et)$_3$NO or mCPBA before addition of substrate.
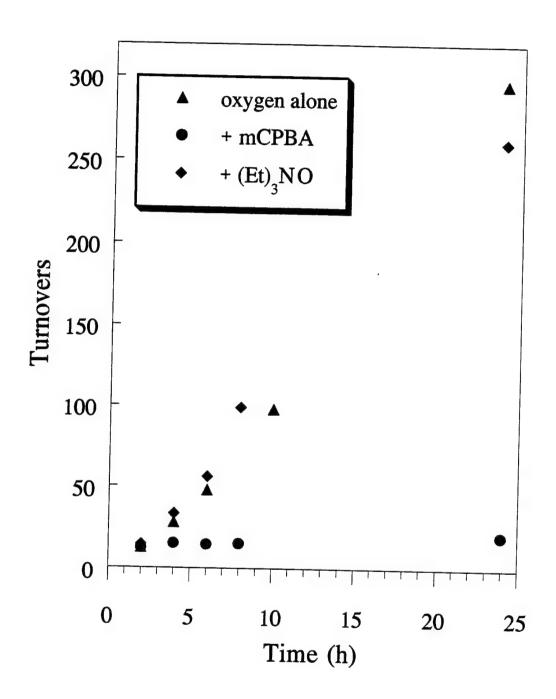
Figure 5.10 -- The relative rates of cyclhexene oxidation after the addition of 10 or 300

equivalents of TBHP. Although a small addition of peroxide only induces

a minor enhancement of the chemistry, the large addition appears to

initiate a free radical reaction that may not be related to the ruthenium

catalyst.
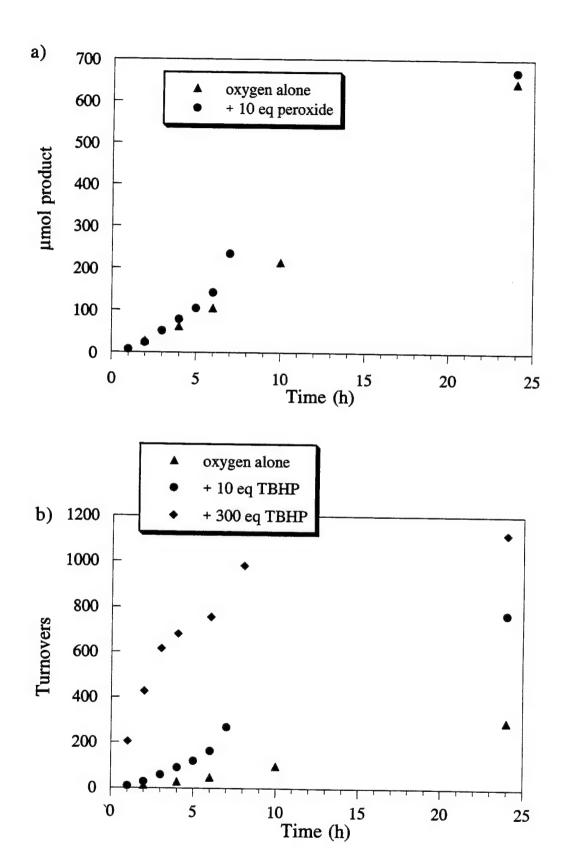
Figure 5.11 -- Relative turnovers in experiments stirred at two different rates indicate that phase transfer was not rate limiting. Experiments that were stirred more slowly showed slightly more activity than average.
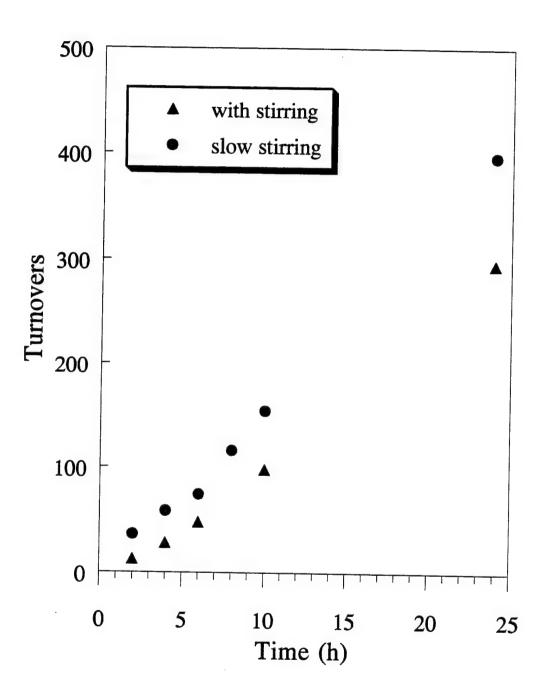
Figure 5.12 -- Relative rates of cyclohexene oxidation under dioxygen or under a mixture

of oxygen and carbon monoxide, indicating that CO does not inhibit

catalysis by $Ru^{II}TFPPCl_8(CO)$.
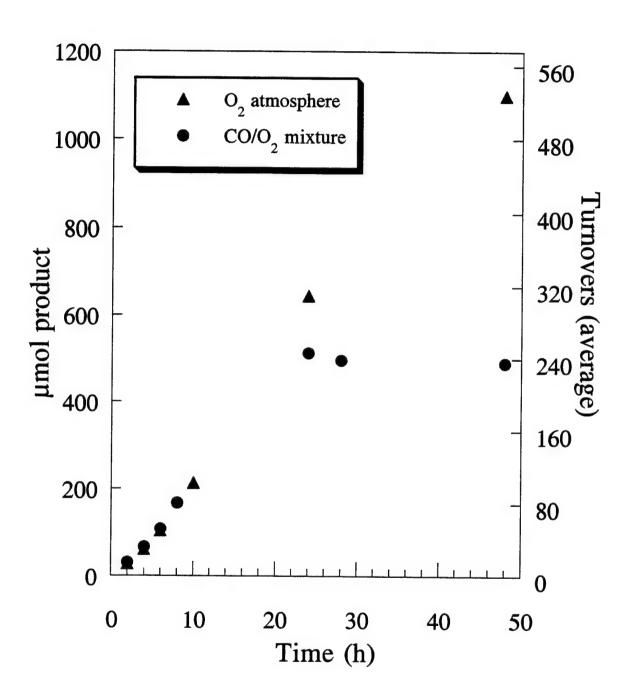
Figure 5.13 -- UV-Vis spectrum of Ru^{II}TFPPCl$_8$(CO) in carbon tetrachloride after two

days in a Parr reactor under 1100 psi of carbon monoxide. The Soret band

is slightly red shifted and the Q bands are slightly blue shifted from the

spectrum before the Parr reactor. The absorption at 280 nm is believed to

be from an organic product (see text).
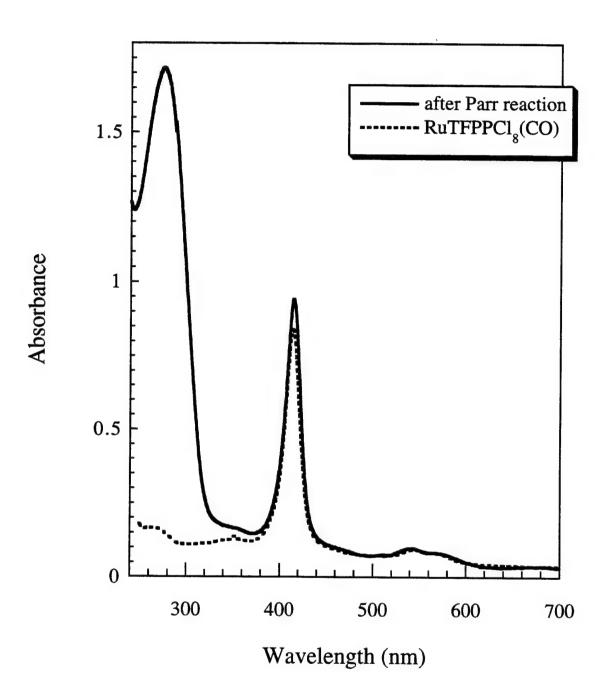
Figure 5.14 -- Relative rates of cyclohexene and cyclohexene-d_{10} oxidation by Ru^{II}TFPPCl$_8$(CO) with dioxygen.
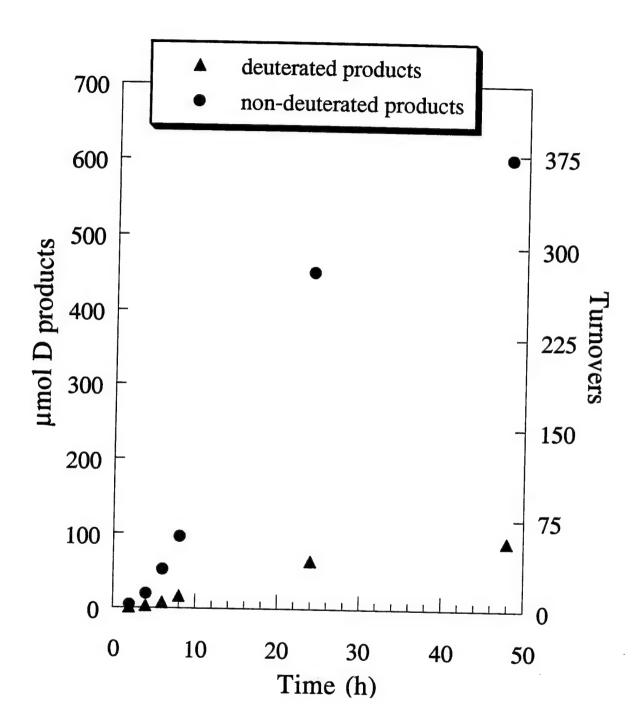
Figure 5.15 -- Cyclohexene oxidation experiments carried out in the dark showed great
variability in the initiation period. Eventually both reactions showed
significant reactivity.
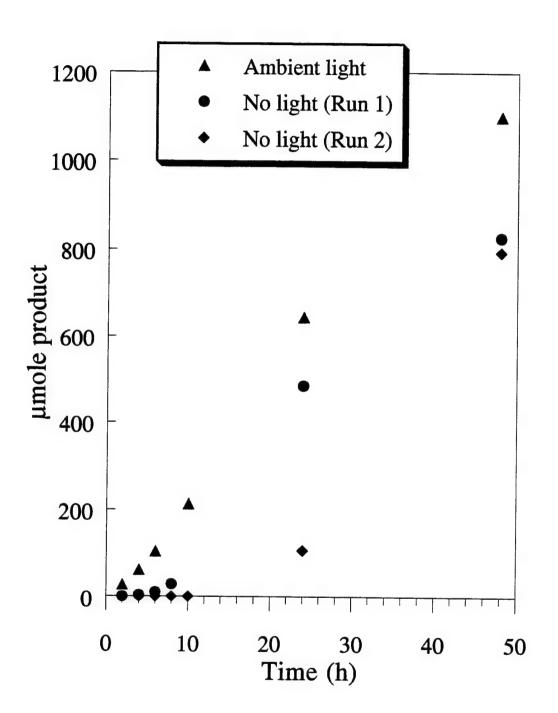
Figure 5.16 -- Photolysis of a cyclohexene oxidation reaction by $Ru^{II}TFPPCl_8(CO)$ with dioxygen with a tungsten lamp dramatically increased the reaction rate.
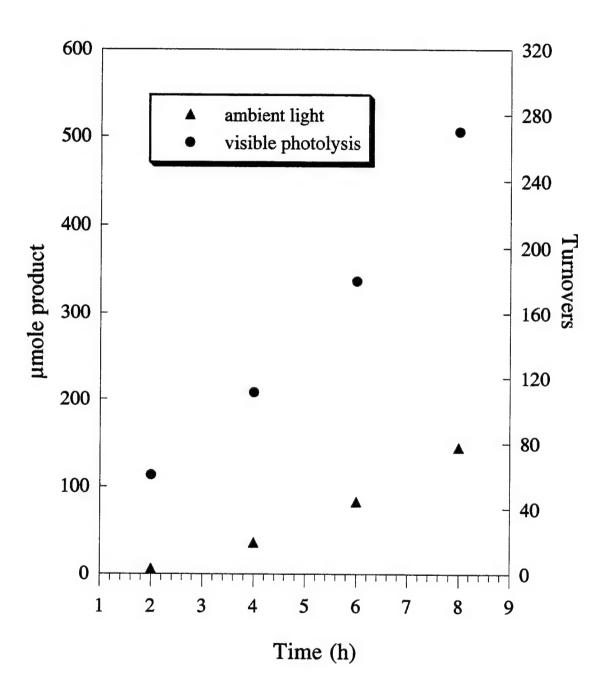
Figure 5.17 -- Transient absorption spectrum in the Q band region immediately following irradiation at 480 nm. The appearance of a low energy band is consistent with formation of a porphyrin triplet excited state.
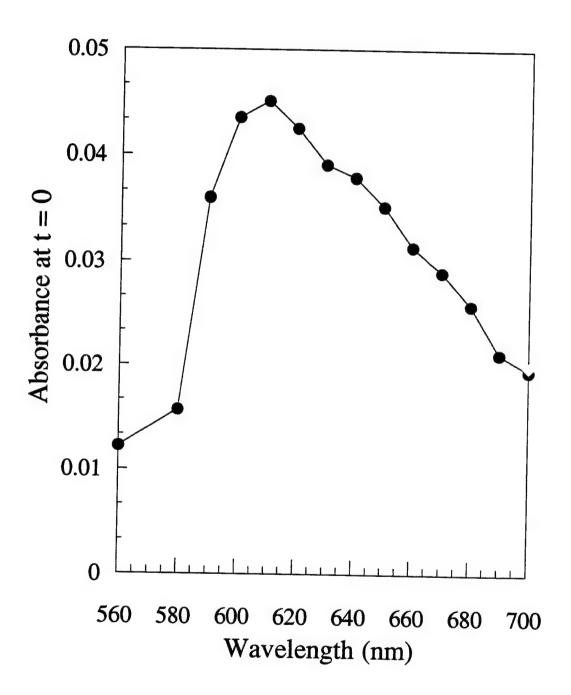
Figure 5.18 -- A 5 μs transient spectrum at 415 nm for excitation of $Ru^{II}TFPPCl_8(CO)$

with 355 nm light. The sample is in methylene chloride and under an

atmosphere of CO. Other transient spectra are in appendix 5.

DATA FILE: RUCO.006   1995-2-23   9:27:49
TIME RANGE: 5.0 μs   INPUT V RANGE: 0.320V   INPUT OFFSET: 0 %
EXPERIMENT: TRANSIENT ABSORBTION
FAST (200 MHz) QUASI-DIFFERENTIAL AMP
                            MODE: SINGLE-ENDED

SHOTS PRE CYCLE: 10   CYCLES: 5   PMT VOLTIGE: 702 V
EXCITATION WAVELENGTH: 355 nm   OBSERVATION WAVELENGTH: 415 nm
SAMPLE: RuCl8(CO)
SOLVENT: CH2Cl2
TEMPERATURE: rt
COMMENT: under CO
COMMENT:

---> FIXED PARAMETER;   ! ---> FIXED SIGN

$$y(t) = C0 + C1*e^{-k1*t} + C2*e^{-k2*t}$$

C0 = -1.941E-2
C1 = -1.023E-1   !k1 = 3.951E6 s^{-1}
C2 = -4.168E-2   !k2 = 8.530E5 s^{-1}
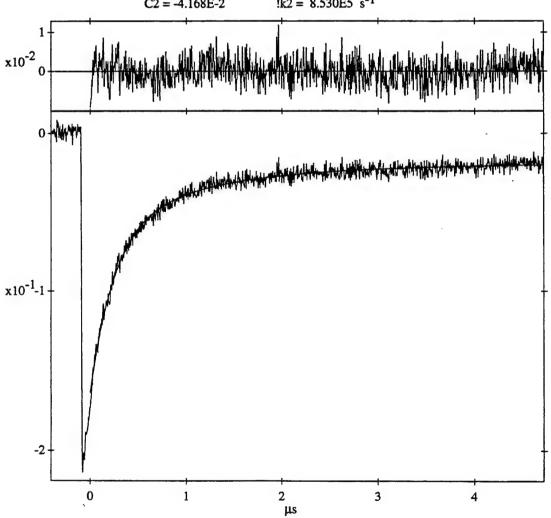
Figure 5.19 -- A 50 µs transient spectrum at 415 nm for excitation of $Ru^{II}TFPPCl_8(CO)$

with 355 nm light. The sample is in methylene chloride and under an

atmosphere of CO. Other transient spectra are in appendix 5.

DATA FILE: RUCO.002   1995-2-23   8:56:56
TIME RANGE: 50 μs   INPUT V RANGE: 0.320V   INPUT OFFSET: 0 %
EXPERIMENT: TRANSIENT ABSORBTION
FAST (200 MHz) QUASI-DIFFERENTIAL AMP
                            MODE: SINGLE-ENDED

SHOTS PRE CYCLE: 10   CYCLES: 5   PMT VOLTIGE: 700 V
EXCITATION WAVELENGTH: 355 nm   OBSERVATION WAVELENGTH: 415 nm
SAMPLE: RuCl8(CO)
SOLVENT: CH2Cl2
TEMPERATURE: rt
COMMENT: under CO
COMMENT:

---> FIXED PARAMETER;   ! ---> FIXED SIGN

$$y(t) = C0 + C1*e^{-k1*t} + C2*e^{-k2*t}$$

C0 = -7.483E-3
C1 = -7.385E-2   !k1 = 2.196E6 s^{-1}
C2 = -2.381E-2   !k2 = 1.318E5 s^{-1}

μs
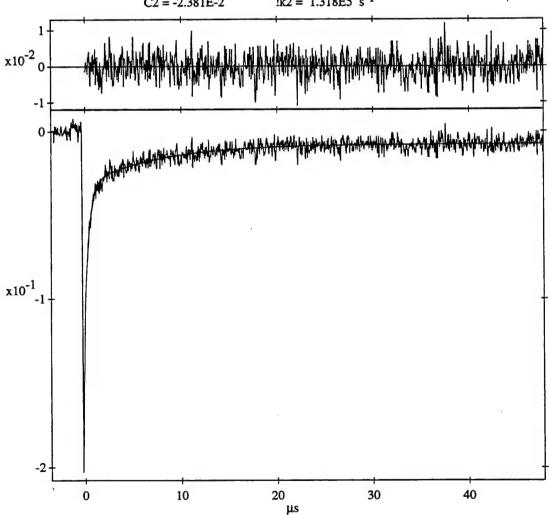
Figure 5.20 -- The 50 µs transient absorption spectrum after excitation with 355 nm light
of equally concentrated solutions of RuTFPPCl$_8$(CO) in methylene
chloride under different atmospheres. The spectra are very similar; only
the ethylene spectrum has a larger decrease in Soret intensity relative to
the other samples.
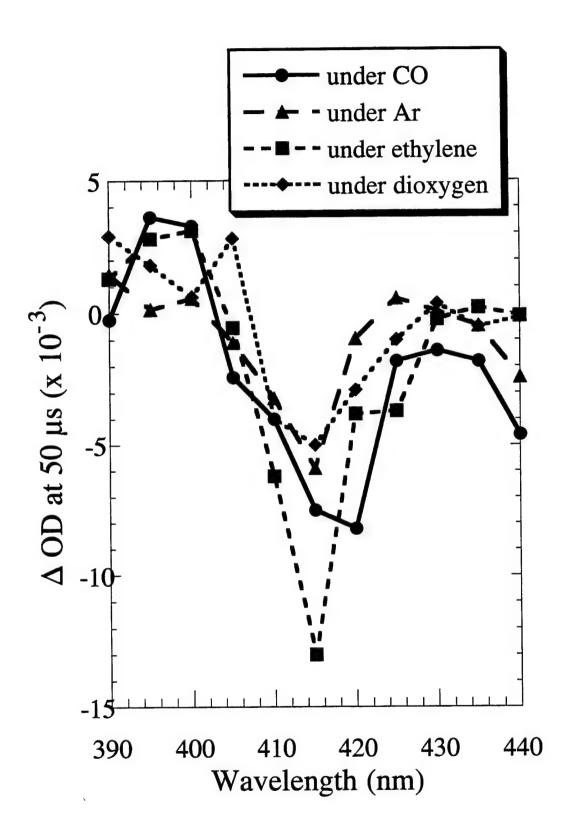
Figure 5.21 -- UV-Vis spectra of the samples shown in Figure 5.20 after the completion

of the laser photolysis experiments. The samples under argon and

dioxygen show significant broadening and a decrease in the Soret

intensity, but CO or ethylene atmospheres protected the porphyrin from

decomposition.
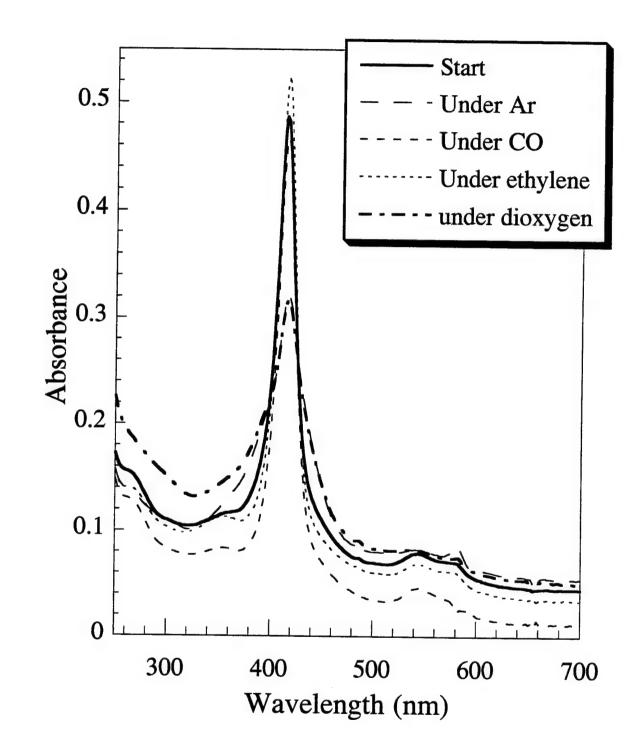
Figure 5.22 -- A mechanism for catalytic olefin oxidation by RuTFPPCl$_8$(CO) with

dioxygen involving an excited state of the porphyrin. Olefin binding is

enhanced in the excited state due to the photochemical oxidation of the

metal. The excited state could also be quenched by oxygen, forming

singlet oxygen that could also lead to product formation.

$\diagup\!\!\!\!=\!\!\!\!\diagdown$ = olefin
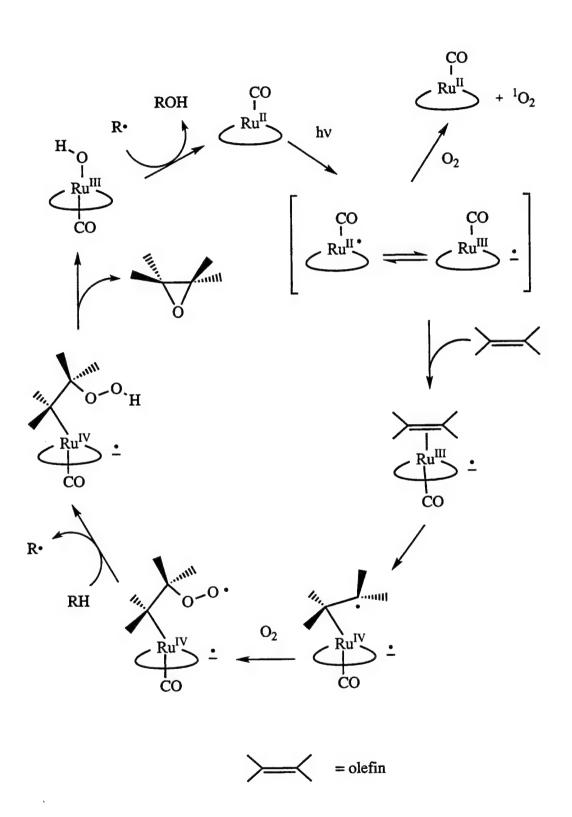
Table 5.1. Oxidation Chemistry with RuTFPPCl$_8$(CO).

Reaction Conditions[a]	% (epoxide)	% (OH)	% (O)	Turnovers
PhIO	42	56	2	9.9
O$_2$	15	58	27	296
O$_2$ + 10 eq (Et)$_3$NO	7	59	35	260
O$_2$ + 5 eq mCPBA	35	52	13	20
O$_2$ + 10 eq TBHP	14	54	32	770
O$_2$ + 300 eq TBHP	7	65	28	1119
slow str rate	14	61	25	258
CO/O$_2$	7	57	36	258
No light	16	59	25	200 (average)
Visible Photolysis	15	61	24	531

a. Reactions run in 15 mL of methylene chloride with approximately 1.5 - 2.0 μmol of RuTFPPCl$_8$(CO) and 1 mL of cyclohexene. All reactions were run under 1 atm of dioxygen, except the PhIO reaction, which was under an argon atmosphere. See text and experimental section for more details.

Chapter 6

Solubility and Reactivity
of Iron and Ruthenium Halogenated Porphyrins
in Supercritical Carbon Dioxide

Introduction

The investigation of biomimetic metalloporphyrin catalysis has two general long range goals: first, to better understand oxidation chemistry *in vivo*, and second, the more economic objective of applying this knowledge to the design of efficient oxidation catalysts for industrial applications. The latter aim of efficiency is not specific to oxygenation, but also drives research in other areas of catalysis. Increasing pressure from the government to reduce waste as well as burgeoning costs of waste disposal have necessitated fundamental changes in catalysis methodology. Consideration of the catalyst efficiency and longevity are no longer sufficient; solvent disposal, waste stream reduction, and chemical toxicity are of increasing importance.

Supercritical carbon dioxide (SC CO_2) has recently received great attention as an environmentally friendly solvent. Non-toxic, inexpensive, and nonflammable, it is currently used for commercial extraction of hops and decaffination of coffee.[1] SC CO_2 is being further explored as a medium for uses ranging from the extraction of lanthanides from nuclear reprocessing waste[2] to dry-cleaning.[3] The primary applications and research related to SC CO_2 have focused on separation technology. The use of supercritical carbon dioxide as a solvent for chemical reactions has not been widely explored, an area where the unique attributes of supercritical fluids (SCFs) could possibly affect the desired enhancements in catalysis.

In general, SCFs have properties that range between those of gases and liquids. Gases are miscible in SCFs, eliminating phase transfer problems during hydrogenation or oxygenation catalysis in homogeneous solution. The density of a SCF is extremely

dependent on the pressure and temperature, and can vary between being "gas-like" or "liquid-like". The polarity of SC CO_2 is similar to that of halogenated hydrocarbons, indicating that it may be an excellent replacement for hazardous solvents such as carbon tetrachloride or methylene chloride.[4]

Carbon dioxide has an unusually low critical point. A phase diagram (Figure 6.1) shows the critical point at 72.8 atm and 31 °C, which is far lower than that of water (218 atm and 374 °C).[5] These conditions are easily achievable in the laboratory, albeit with care and respect, and are also feasible for industrial applications.

Supercritical carbon dioxide has recently begun to be explored as a medium for catalysis. DiSimmone conducted the free radical polymerization of methyl methacrylate in SC CO_2. High yields of quality poly(methyl methacrylate) were obtained from a single phase reaction, avoiding the aqueous and organic dispersing media used in classical polymerization techniques.[6] Noyori et. al. have achieved formation of dimethylformamide from hydrogen gas, dimethylamine, and supercritical carbon dioxide with a ruthenium phosphine catalyst. The CO_2 serves as both solvent and reactant, driving the reaction at a rate an order of magnitude above that in an organic solvent.[7] Similarly, the miscibility of H_2 in SC CO_2 leads to very high initial rates of reaction for the formation of formic acid, catalyzed by $Ru(PMe_3)_4(H)_2$.[8] Asymmetric hydrogenation reactions with ruthenium and rhodium catalysts have demonstrated that enantioselectivity can be increased by moving from a conventional solvent to supercritical CO_2.[3] The above examples demonstrate several methods in which SCFs have improved catalytic processes.

Despite these recent successes, only one oxidative system has been investigated in SC CO_2.[9] The uncatalyzed free radical oxidation of cyclohexane with dioxygen in SC CO_2 has been reported. The conversion of cyclohexane and the ratio of cyclohexanol and cyclohexanone produced are controlled by the pressure and temperature near the critical region.[10] No other oxidations in supercritical carbon dioxide have been reported. Catalytic olefin oxidation by halogenated metalloporphyrins seems an ideal system for analysis in

SC CO_2. Since dioxygen is the only additive in these reactions (no coreductant is needed), the miscibility of O_2 with SC CO_2 has potential to increase reactivity in the SCF. Furthermore, the different solvation properties of SC CO_2 could lead to different selectivity in the oxidation reactions.

Before investigating reactivity, we determined the solubility of three halogenated porphyrins in SC CO_2. Although the dielectric constant of supercritical carbon dioxide increases with pressure, it remains quite low (only 1.8 at 2000 psi), making SC CO_2 a rather poor solvent.[4] However, since chlorinated solvents able to dissolve halogenated porphyrins (i.e., CCl_4) also have low dielectric constants, the porphyrins were anticipated to be soluble in the supercritical medium. Fe(TFPP)Cl, Fe(TFPPBr$_8$)Cl and RuTFPPCl$_8$(CO) were investigated, since their chemistry in methylene chloride had been previously studied in our laboratory.

Results

Solubility Studies

An apparatus allowing UV-Vis spectroscopy under high pressures is pictured in Figure 6.2. A tank of liquid carbon dioxide was connected to allow flow directly into the cell or into an ISCO syringe pump, which is capable of condensing CO_2 up to 5000 psi. The cell was secured with a stand on top of a stirplate in between the lamp and detector. Rubber heating tape was wrapped around the cell to maintain the temperature at 40°C during the UV-Vis experiments (Figure 6.2).

After the cell was aligned in the spectrophotometer setup, a solution of porphyrin in methylene chloride was injected into the cell through the thermocouple inlet. The thermocouple was then reattached, and the cell evacuated to remove the organic solvent. CO_2 was added, and the absorbance calculated from light intensity measurements taken at 500 psi intervals (Figure 6.3-6.6). A spectrum of each compound in methylene chloride is also displayed in each figure for comparison. The concentration of porphyrin in solution is

calculated assuming the extinction coefficients are similar in methylene chloride and in SC CO_2. Although porphyrin spectra are known to be sensitive to solvent, generally the position of the band shifts more than the extinction coefficient.

In general, solubility was found to increase with pressure. Although the spectra are quite noisy, due to refraction from mixing lines in the large cell, the main features of the porphyrin are still observable. Fe(TFPP)Cl (Figure 6.3) is the least sensitive to pressure, but has the highest solubility, with the concentration only changing from 0.27 to 0.30 μM from 2000 to 5000 psi CO_2. The Q band region is most distinct in these spectra, with a shoulder at 500 and a stronger band at 610 nm corresponding to the solution spectrum bands at 504 and 620 nm.

The resolution of the Soret band of Fe(TFPPBr$_8$)Cl is lost in SC CO_2 (Figure 6.4). However, there is a definite increase in absorbance from 1400 to 3500 psi, and the solubility increases from 0.07 to 0.20 μM. Further increases in pressure do not cause much change in absorbance.

Unlike the iron porphyrins, the Soret band of RuTFPPCl$_8$(CO) is quite distinct in SC CO_2. The Q band region in this spectrum, however, has a substantial amount of instrument noise (Figure 6.5). The solubility increased from almost nothing in liquid carbon dioxide (800 psi) to 0.16 μM (5000 psi). The changes of solubility with pressure for all three porphyrins are plotted in Figure 6.6. Although none of the porphyrins were soluble in liquid CO_2 (data not shown), all of them were soluble once the critical point was achieved (> 1200 psi). Surprisingly, little change in the concentration was observed at higher pressures.

Solubility Studies Discussion

The solubility of halogenated porphyrins in supercritical carbon dioxide was significantly less than in halogenated solvents. Although solubility increased with pressure as the dielectric constant increased (became more like that of a halogenated solvent), the

maximum solubility achieved was quite low (< 1 μM). Presumably SC CO_2 never became polar enough to dissolve large amounts of porphyrin.

The observed pressure broadening of electronic absorption bands is not unexpected. The $d\sigma^* \rightarrow p\sigma$ transitions in single crystals of Pt_2Cl have been shown to red shift and broaden with pressure.[11] However, the rather dramatic change in the shape of the spectrum from room temperature and one atmosphere pressure relative to SC pressure and temperature for both of the iron porphyrins is rather puzzling. The loss of resolution in the Soret bands of Fe(TFPP)Cl and Fe(TFPPBr$_8$)Cl could be ascribed to pressure broadening. Other aspects of the spectra are not as readily explained. A single intense Q band has appeared in the spectrum of Fe(TFPPBr$_8$)Cl; although absorption maxima often shift with solvent, the appearance of a new absorptions suggests that the porphyrin has been chemically altered. A blue shift in the Soret band and an increase in intensity of a band around 600 nm may be attributed to dimerization at high pressures. Relative to the 410, 510, and 620 nm bands in Fe(TFPP)Cl, (FeTFPP)$_2$O has absorption bands at 398 and 600 nm; these values match well with the observed SC CO_2 spectrum (λ_{max} = 390, 610 nm). Similarly, a μ-oxo dimer of Fe(TFPPBr$_8$)Cl would be expected to have a blue shifted Soret band and a more intense Q band relative to the monomer. The SC CO_2 spectrum of Fe(TFPPBr$_8$)Cl has maximum absorbance at 420 and 600 nm, relative to a 442 nm Soret band and weak Q bands in the solution spectrum. Although formation of a μ-oxo dimer should not have been possible in these experiments, since no oxygen was present in the cell, other dimerization modes are possible and could also account for the observed spectral changes. Contaminants from the carbon dioxide are also possible; although high purity carbon dioxide should be fairly free of impurities, no scrubbers were used. Dimerization is further suggested by the lack of pressure shifting with RuTFPPCl$_8$(CO); the ruthenium porphyrins are not as susceptible to dimerization as the iron analogs. Higher resolution spectra would have to be obtained to fully address this question.

A second complication was introduced by the use of methylene chloride. Methylene chloride was found to extract plasticizers from the O-rings used to make the seal between the sapphire windows and the cell. When the pressure was decreased, the plasticizers formed a film on the interior of the cell, possibly causing interference patterns and reducing the quality of the spectra. Furthermore, the plasticizers seem to reduce the solubility of $RuTFPPCl_8(CO)$. Addition of $RuTFPPCl_8(CO)$ as a solid to the cell resulted in much high solubility (Figure 6.7). By 3000 psi, the Soret band had already reached the maximum absorbance able to be measured by the instrument (~ 0.4).

Addition of cyclohexene resulted in a higher quality spectrum for $RuTFPPCl_8(CO)$ (Figure 6.8). No solubility is observed in liquid carbon dioxide, but the transition limit of the spectrophotometer is reached by 2000 psi, indicating that cyclohexene is an excellent co-solvent for $RuTFPPCl_8(CO)$. Cyclohexene also reduces the noise level in the ruthenium porphyrin spectrum; this effect is not understood. The structure in the Q band region changes in the presence of olefin, with a slight red shift and different intensity for the Q(1,0) and the Q(0,0) bands relative to the methylene chloride spectrum, indicating that cyclohexene may coordinate at high pressure, since no distinct Q bands were observed with SC CO_2 alone.

Despite the complications and noise levels of the spectra, lower limits for the solubility of the three halogenated porphyrins were determined. The minimal solubility of these complexes is not expected to limit the reactivity of the catalysts in supercritical carbon dioxide since the co-solvent properties of the substrate, cyclohexene, will increase the net solubility of $Fe(TFPP)Cl$, $Fe(TFPPBr_8)Cl$, and $RuTFPPCl_8(CO)$ in the oxidation reaction mixture.

The ability to perform UV-visible spectroscopy at high pressures is a valuable tool for studying reaction intermediates in SCF reactions. This will help determine if reaction pathways change at higher pressures. Further work to enable transient IR and emission spectroscopy in SCF systems is currently in progress at LANL.

Oxidation of Cyclohexene

We investigated the ability of Fe(TFPP)Cl, Fe(TFPPBr$_8$)Cl, and RuTFPPCl$_8$(CO) to oxidize cyclohexene in supercritical carbon dioxide. The oxidation reaction had been studied in methylene chloride (Chapter 4 and 5), providing a comparison for data in a SCF. For oxidations with dioxygen, it was thought that the miscibility of O$_2$ would increase the reaction rate relative to the solution chemistry.

In order to help separate solvent and pressure effects, oxygenation reactions with iodosobenzene as an oxygen source were also investigated. This chemistry should be relatively unaffected by pressure, and should help isolate the different solvation properties at high pressure.

The oxidation reactions were conducted in a small autoclave reactor (Figure 6.9). Constructed in a similar fashion to the UV-Vis apparatus, this system had an additional inlet for pressurized air. The porphyrin, cyclohexene, and iodosobenzene (if used) were added to the reactor, which was then sealed and connected to the carbon dioxide inlet. As with the UV-Vis cell, the system temperature was maintained at 40 °C and the reaction stirred to maintain equilibrium. All reactions were run at 5000 psi of CO$_2$ to maximize solubility of the porphyrin. At the end of the batch reaction, the pressure was let down through a metering valve, and volatile organics were collected in cold acetone. The cell was washed with additional acetone, and products were detected by GC/MS.

Two reactions were run in the UV-Vis cell in order to determine the effect of light on the ruthenium porphyrin oxidation reaction. Since irradiation with visible light dramatically enhances catalysis by RuTFPPCl$_8$(CO) with dioxygen in methylene chloride, we wanted to determine if light would also enhance cyclohexene oxidation in SC CO$_2$.

The results of the oxidation reactions are shown in Figures 6.10 - 6.12. With iodosobenzene, the overall activity was similar to the methylene chloride reactions for Fe(TFPP)Cl and Fe(TFPPBr$_8$)Cl. RuTFPPCl$_8$(CO) activity was considerably higher in

SC CO$_2$, with 21 turnovers compared to only 5 in methylene chloride (4 hour points). The product distributions for these reactions showed more variation. Notably, Fe(TFPP)Cl produced only cyclohexene oxide. For the perhalogenated iron and ruthenium complexes, higher oxidation products were observed. While reactions in methylene chloride have only been found to produce 2-cyclohexen-1-ol and 2-cyclohexen-1-one, the SC CO$_2$ reactions showed large peaks in the GC at later retention times. The first was identified by comparison to a library mass spectrum as 7-oxa-bicyclo[4.1.0]heptan-2-one (Figure 6.13). The second was assumed to be 4-hydroxy-2-cyclohexen-1-one due to a similar relationship in the retention times of cyclohexene oxide and 2-cyclohexen-1-ol, and since it is the logical partitioning product from the oxidation of 2-cyclohexen-1-one. Both Fe(TFPPBr$_8$)Cl and RuTFPPCl$_8$(CO) reactions with PhIO showed less 2-cyclohexen-1-ol than in methylene chloride, and more 2-cyclohexen-1-one, as well as 7-oxa-bicyclo[4.1.0]heptan-2-one and 4-hydroxy-2-cyclohexen-1-ol. None of the reactions used more than 30% of the available oxidant in 4 hours. A batch reaction of Fe(TFPPBr$_8$)Cl run for 12 hours showed no more epoxide formation, but more allylic oxidation products were observed.

With air, the catalyst activities were similar in the two solvents. It is difficult to make a direct comparison, because the batch reactions in SC CO$_2$ were run for different times than the methylene chloride experiments. Nevertheless, it is clear that all catalysts are quite active in the supercritical solvent. Fe(TFPP)Cl (at 4 hours), Fe(TFPPBr$_8$)Cl, and RuTFPPCl$_8$(CO) (at 12 hours) showed 11, 59, and 51 turnovers, respectively. If the higher oxidation products are considered as more than one turnover, the numbers for the latter reactions increase to 127 and 90 turnovers. As with iodosobenzene, substantial amounts of multiple oxidation products were observed in all reactions, with a decrease in the amount of 2-cyclohexen-1-ol produced. Surprisingly, a greater percentage of epoxide was also produced.

Both Fe(TFPPBr$_8$)Cl and RuTFPPCl$_8$(CO) had substantial initiation periods in SC CO$_2$. Batch reactions run for only 4 hours showed no trace of products. After 12

hours, however, significant activity was observed, as described above. Only Fe(TFPP)Cl showed activity with air in the 4 hour time period. Attempts to shorten the initiation period for RuTFPPCl$_8$(CO) by the addition of light were not successful. Two experiments with RuTFPPCl$_8$(CO) were conducted in the larger UV-Vis cell. Upon addition of CO$_2$, the solution turned a bright red, indicating that cyclohexene serves as an excellent co-solvent for the catalyst. A flashlight was used to irradiate the reaction through the cell window for the duration of the batch reaction. However, after only a few hours, the pressure dropped and the solution bleached. A reaction in the UV-Vis cell was attempted twice. The first reaction, with one atmosphere of air, bleached after 20 hours. The second, with 5 atm air, bleached within 6 hours. After bleaching was observed, the cell was let down as previously described. No product formation was detected in either light reaction.

Discussion Oxidation Experiments

The iodosobenzene reactions in supercritical carbon dioxide all showed an increase in the percent epoxide formed relative to reaction in CH$_2$Cl$_2$. As discussed in Chapter 4, epoxidation with a high-valent metal-oxo is believed to occur by a different mechanism than hydroxylation. The different solvation properties of SC CO$_2$ may increase the probability for electron transfer (leading to epoxidation) over hydrogen abstraction (leading to hydroxylation). The success of free radical polymerization reactions conducted in SC CO$_2$ suggests that radicals are quite stable in a supercritical medium. However, the solvent may change the stability of the caged radical species such that electron transfer becomes more favorable. SC CO$_2$ may provide a new medium for probing the oxo-transfer step in olefin oxidation reactions.

In addition to the increase in epoxide formation, there is also an increase in multiple oxidations of the same substrate molecule, both with PhIO and dioxygen. The supercritical fluid did not greatly increase the observed turnover numbers, suggesting that phase transfer is not the limiting step in the dioxygen reactions for any of the porphyrins. However, the

different solvent properties of SC CO_2 may be changing the selectivity; perhaps the catalysts are more soluble in the oxidized cyclohexene derivatives than in cyclohexene itself. Therefore, the catalyst could re-oxidize a single substrate multiple times before encountering other substrate molecules.

For $RuTFPPCl_8(CO)$, fewer turnovers are observed in the dark cell, consistent with the photochemical reaction mechanism described in Chapter 5. However, the UV-Vis suggests a greater interaction between the porphyrin and substrate in SC CO_2, indicating that olefin binding may occur in the ground state in this medium, whereas it only is effective in the excited state in a methylene chloride solution. Alternatively, a different reaction mechanism may take precedence in this solvent. Unfortunately, attempts to photolyze the reaction were complicated by the cell design. The Buna-N O-rings used to seal the sapphire windows, while having excellent resistance to supercritical carbon dioxide, are reported to have unsatisfactory resistance to alkanes,[12] suggesting that the "bleach" observed upon photolysis was not due to porphyrin decomposition but a leaking cell.

Conclusion

The preliminary results described above demonstrate that supercritical carbon dioxide is an adequate solvent replacement for methylene chloride for porphyrin-catalyzed oxidation of cyclohexene. Large rate enhancement was not observed, but changes in the reaction selectivity did occur. Most notable was the 100% selectivity observed for epoxidation of cyclohexene with Fe(TFPP)Cl and PhIO, and increased epoxidation selectivity for both $RuTFPPCl_8(CO)$ and $Fe(TFPPBr_8)Cl$ in reactions with either PhIO or O_2. For allylic oxidation products, multiple oxidations of the same substrate molecule was observed, suggesting that destruction of organics in a supercritical medium may be favorable under different conditions. A repeat of the oxidation experiments at different temperatures and pressures would reveal if the selectivity could be tuned to favor one

pathway more completely. Further experiments would be needed to determine the source of these effects.

Methods

RuTFPPCl$_8$(CO) and Fe(TFPPBr$_8$)Cl were synthesized as in Chapter 2. Fe(TFPP)Cl was used as received (Aldrich). Cyclohexene was from Aldrich, and distilled under argon before use. Acetone and methylene chloride were used as received from EM Science. Iodosobenzene was from TCI and used as received. Air and carbon dioxide were from Albuquerque Welding. Oxidation products were determined by injection onto an Hewlett Packard GC/MS with an auto injector and a JW Scientific DB-5 30m column. Sample identification was determined by injection of an authentic sample for cyclohexene oxide, 2-cyclohexen-1-ol, and 2-cyclohexen-1-one (Aldrich). The identity of one higher boiling peak was determined by the library on the GC MS.

Standard NPT, Swagelock, and HiP pressure rated valves and connections were used to build the high pressure systems. Stainless steel tubing (1/16" - 1/4") was used for longer connections. An ISCO brand syringe pump was used to pressurize the carbon dioxide. All systems were barricaded behind Lexan shielding, and tubing and valves were secured to the work tables to minimize damage in case of a pressure failure. All systems were equipped with relief valves or rupture discs, so the system would blow at the designed weak point in case of over-pressurization.

UV-Vis spectra were measured on a Hewlett Packard 8452 spectrophotometer. The lamp and detector were removed from the instrument cavity and placed on a laser table to allow room for the large cell. Additional focusing mirrors were placed after the lamp and before the detector to increase light intensity. Intensity data was collected in ASCII format, and loaded onto a Macintosh computer, where absorbance readings were calculated (A = log (I_0/I). I_0 readings were taken at each pressure since the absorbance of CO_2 was found to change considerably around the supercritical transition. This is due to the variable

density of SC CO_2; the change in the index of refraction between the cell windows and solvent decreased at higher pressures. The stirplate was turned off when spectra were taken, in order to minimize refraction by mixing lines in solution. The large cell volume ($\approx$ 75 mL) made it difficult to maintain a constant temperature in the cell, causing visible sheer lines due to the temperature gradient in solution. Averaging intensity data helped decrease the noise in the spectra.

The cell used for UV-Vis experiments was constructed of 316 stainless steel, with a 13.2 cm path length and 1 inch aperture on each side. The seal between the 1 cm thick sapphire windows and the metal cell was made by a Buna-N rubber O-ring, which was replaced after each use. The cell had three inlets for a thermocouple, an inlet valve, and a t-joint which contained a relief valve, an analog pressure gauge, and an outlet line. The outlet could be directed to a vacuum pump or vented to a hood.

For each sample, the cell was first mounted on the stand and aligned for maximum lamp intensity. A solution of porphyrin in methylene chloride was added through the thermocouple inlet, and then the thermocouple was fastened down. By this method, a known amount of porphyrin could be added, such that the possible absorbance in a 13.2 cm path length cell would not be above 1. The cell was evacuated, removing the solvent, and then carbon dioxide was added. The cell was sealed off at each pressure, and allowed to equilibrate to 40 ± 0.5 °C for each intensity reading. Alternatively, excess solid porphyrin was added to the cell before the windows were sealed down (the large nuts for the windows had to be tightened down on a vise).

Oxidation reactions were conducted in a cell designed by Dave Morgenstern and Sam Borkowsky at Los Alamos National Laboratory. This cell was a single 2.5" cylinder of 316 stainless steel, with a 5/8" hole bored into the center. The only openings were for a rupture disc (rated to 10000 psi), an analog pressure gauge, a thermocouple, and the main reactor valve. The total cell volume was $\approx$ 12 mL. The inlet lines allowed the sequential addition of compressed air and carbon dioxide to the cell. Air was always added first, so

that the CO_2 would flush any oxygen from the lines before the system was brought up to pressure. Although air or pure oxygen gas could be used with this reactor, air was used for safety reasons.

Solid porphyrin, cyclohexene, and iodosobenzene (if used) were added to the reactor, the valve was sealed on the vise, and the reactor was then attached to the inlet and letdown tubing. Air was added first, up to the pressure of the tank (110 psig) and then CO_2 up to 5000 psi. As with the UV-Vis experiments, the cell rested on a stirplate and the cell temperature was maintained at 40 °C with heating tape. As soon as the pressure reached 5000 psi, the main reactor valve was closed, and the system allowed to stir for the desired reaction time.

Oxidation reactions were let down by a HiP metering valve through 1/16" tubing, and the end of the tubing was crimped with a hammer to reduce the flow rate. The pressure was let down slowly over a period of 1-2 hours into a vial containing approximately 20 mL of cold acetone to catch volatile organics. The vial rested in a cold block of steel to maintain its temperature and reduce loss of organics. The reaction vessel was then opened and rinsed with acetone to remove residual cyclohexene and products. The rinse was collected, and the volume measured. An aliquot was taken, diluted with a known amount of toluene in acetone to standardize the GC/MS analysis, and injected onto the GC. Although there is undoubtedly some loss to evaporation, it is believed that most of the organic products are collected by this method. No mass balance calculation was attempted.

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Figure 6.1 -- Phase diagram of carbon dioxide (modified from reference 5). The critical
point of CO_2 is at relatively low temperature and pressure, facilitating its use
as a supercritical solvent.

Phase Diagram of Carbon Dioxide

Pressure (atm)

$P_c = 72.8$

$P_3 = 5.1$

Critical point

Solid

Liquid

Gas

Triple point

$T_3 = -56.6$ $T_c = 31$

Temperature (°C)
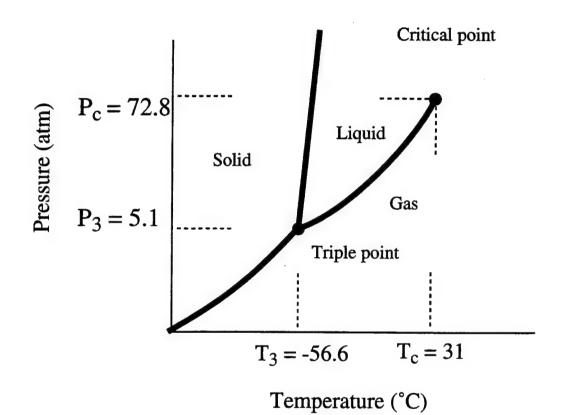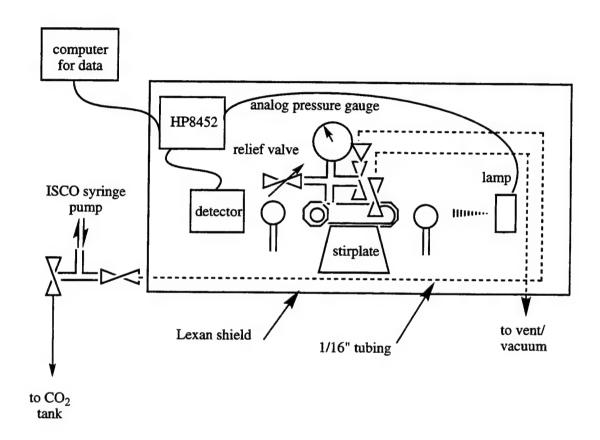
Figure 6.2 -- Apparatus used for UV-Visible spectroscopy in supercritical carbon dioxide.

UV Vis in Supercritical CO$_2$

Cell characteristics: 6 inches long, 13.2 cm path length
1 inch diameter aperture with sapphire windows
75 mL cell volume, including dead space
316 stainless steel
rated to 5000 psi

Figure 6.3 -- Spectra of Fe(TFPP)Cl in methylene chloride and carbon dioxide. The spectrum in SC CO_2 is smoothed to remove noise from refracted light. The solubility did not change much with pressure, increasing only from 0.27 to 0.30 μM from 2000 to 5000 psi of CO_2.
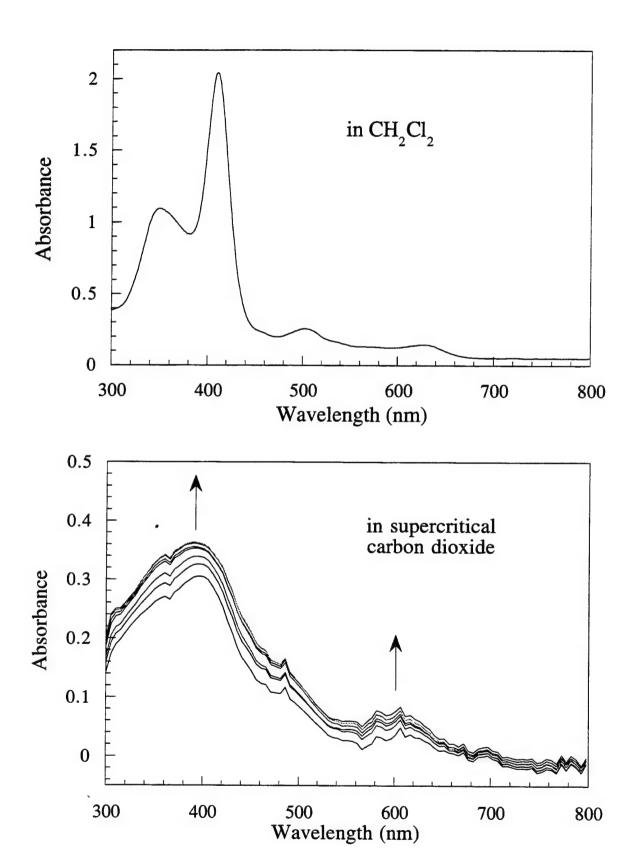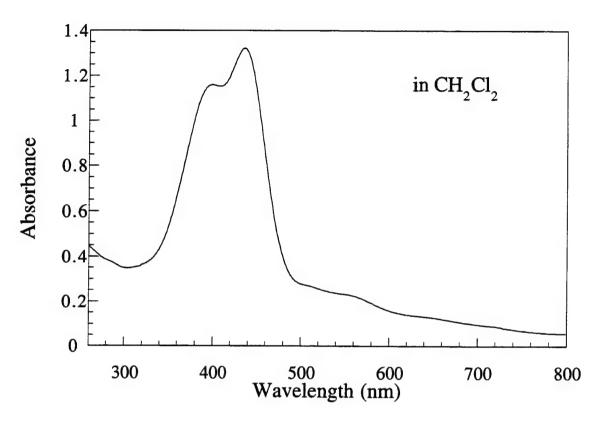
Figure 6.4 -- Spectra of Fe(TFPPBr$_8$)Cl in methylene chloride and carbon dioxide. The

spectrum in SC CO$_2$ is smoothed to removed noise from refracted light. The

solubility increased from 0.07 to 0.20 μM from 2000 to 3500 psi of CO$_2$,

remaining fairly constant after this pressure.
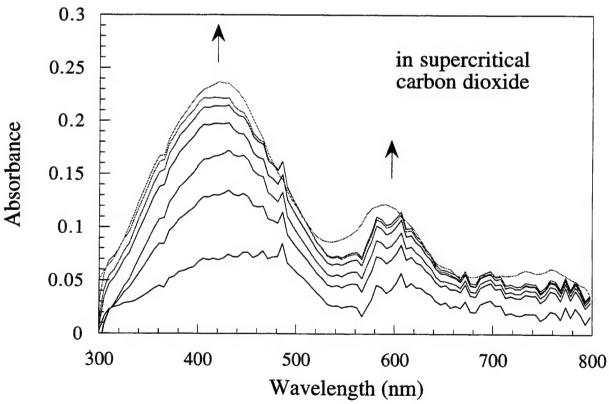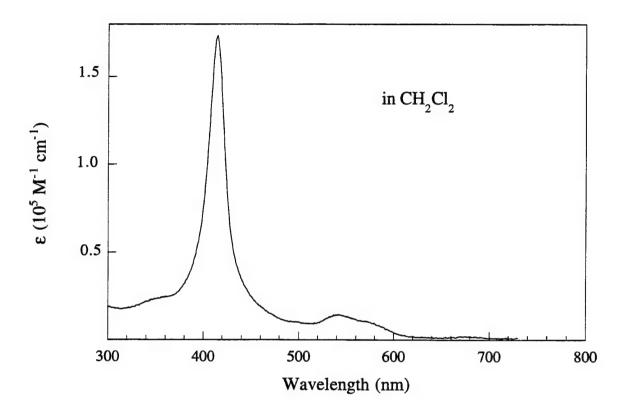
Figure 6.5 – Spectra of RuTFPPCl$_8$(CO)in methylene chloride and carbon dioxide. The

porphyrin is almost insoluble in liquid CO_2, but solubility increased to

0.16 μM at 5000 psi of CO_2. The spectra in the two different solvents match

best for RuTFPPCl$_8$(CO), suggesting no unusual interactions in the

supercritical solvent.
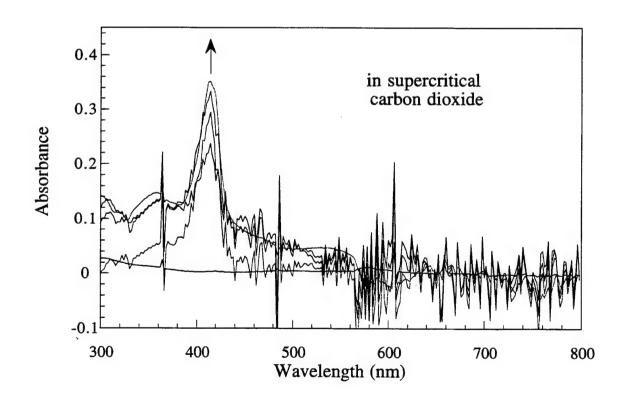
Figure 6.6 -- A plot of solubility versus pressure for the halogenated porphyrins.
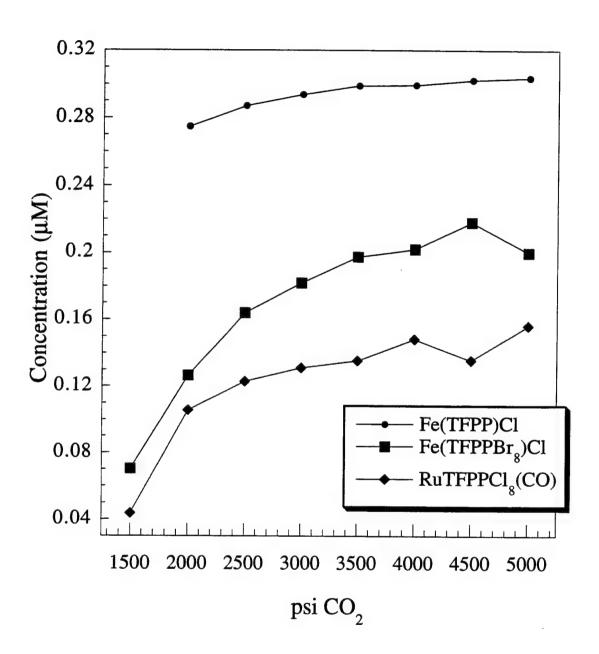
Figure 6.7 -- Spectrum of RuTFPPCl$_8$(CO) in carbon dioxide. This differs from the
spectrum in Figure 6.3 in that the porphyrin was added as a solid, and not as a
methylene chloride solution. The solubility is much higher in this case,
reaching the maximum transmission of the instrument by 3000 psi, suggesting
that a deleterious interaction occurs when the porphyrin is added as a CH$_2$Cl$_2$
solution (data at 2000, 3000, and 4000 psi).
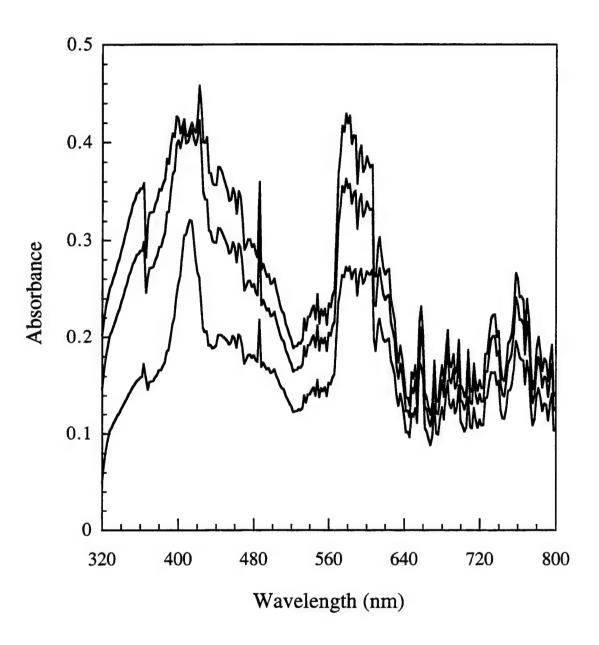
Figure 6.8 -- Spectrum of RuTFPPCl$_8$(CO) with cyclohexene in carbon dioxide. The Q band structure is significantly different than without cyclohexene, suggesting a possible interaction or binding of alkene in the supercritical solvent (data at 800, 1200, 2000, 3000, 4000, and 5000 psi).
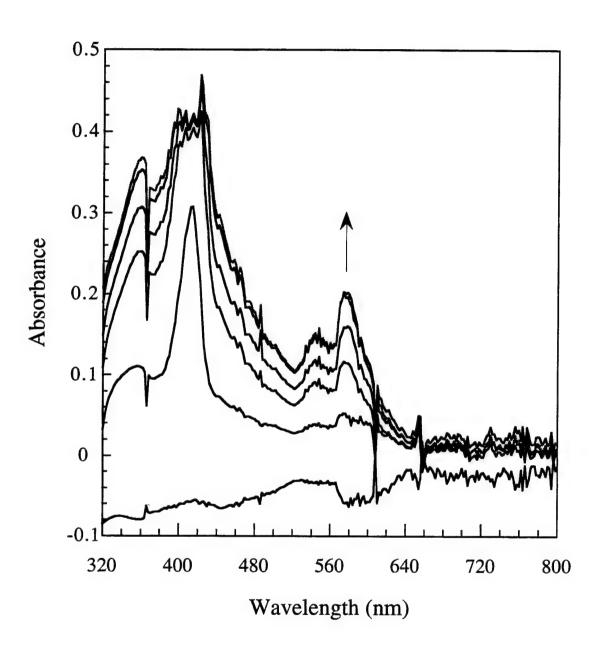
Figure 6.9 -- Cell used for oxidation reactions with iodosobenzene or air by halogenated porphyrins in supercritical carbon dioxide.

Plumbing for High Pressure
Oxygen Reactions in Small Cell

CO$_2$ from ISCO
syringe pump

analog pressure gauge

relief valve

bleed valve

Reactor is 1/2" stainless
steel. Main reactor and valves
are surrounded by a Lexan
explosion shield.

1/4" tubing

shutoff
valve

1/16" tubing   1/8" tubing

sample letdown
into acetone

air inlet

metering
valve   reactor
valve   check
valve

analog pressure gauge

rupture disc (10,000 psi)

thermocouple

stirplate

reactor wrapped with heating tape
to maintain temperature at 40°C

Figure 6.10 -- Turnovers of cyclohexene observed in oxidation reactions with Fe(TFPP)Cl and either iodosobenzene (left) or dioxygen (right). PhIO data is after 4 hours, and the dioxygen results are at 24 hours (CH_2Cl_2) or 12 hours (SC CO_2) in the different solvents. 100% selectivity for epoxide formation is observed with PhIO in SC CO_2.
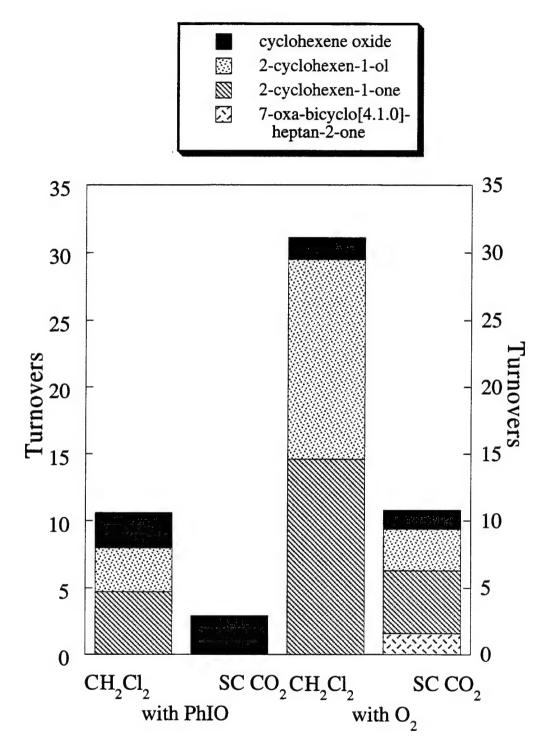
Figure 6.11 -- Turnovers of cyclohexene observed in oxidation reactions with Fe(TFPPBr$_8$)Cl and either iodosobenzene (left) or dioxygen (right). PhIO data is after 4 hours, and the dioxygen results are at 24 hours (CH$_2$Cl$_2$) or 12 hours (SC CO$_2$) in the different solvents. Higher selectivity for epoxide formation is observed with dioxygen in SC CO$_2$ relative to CH$_2$Cl$_2$. Significant amounts of higher oxidation products are also observed.
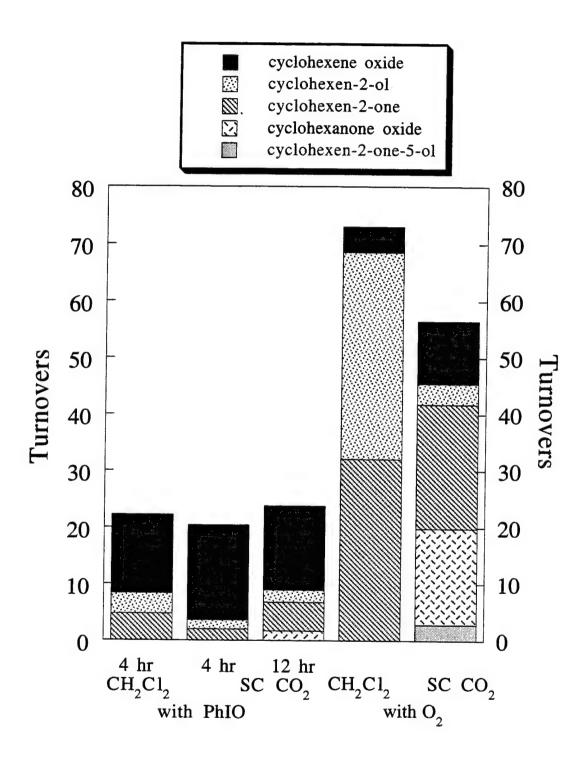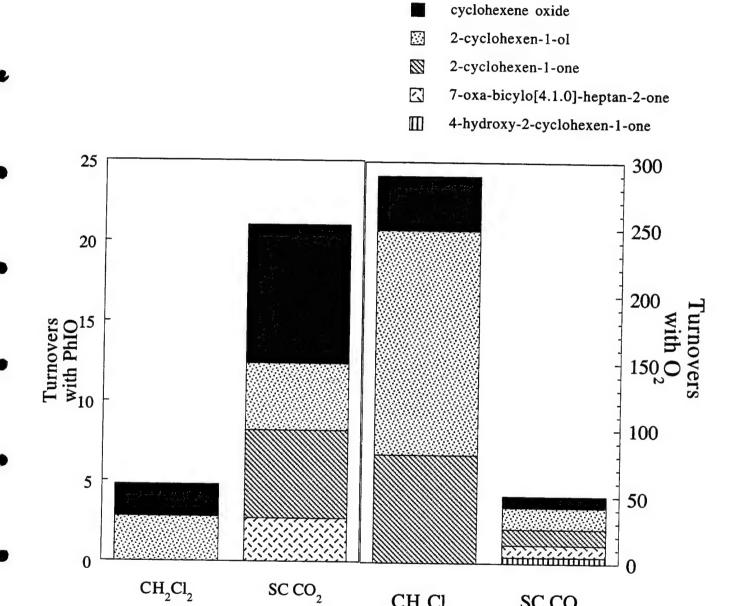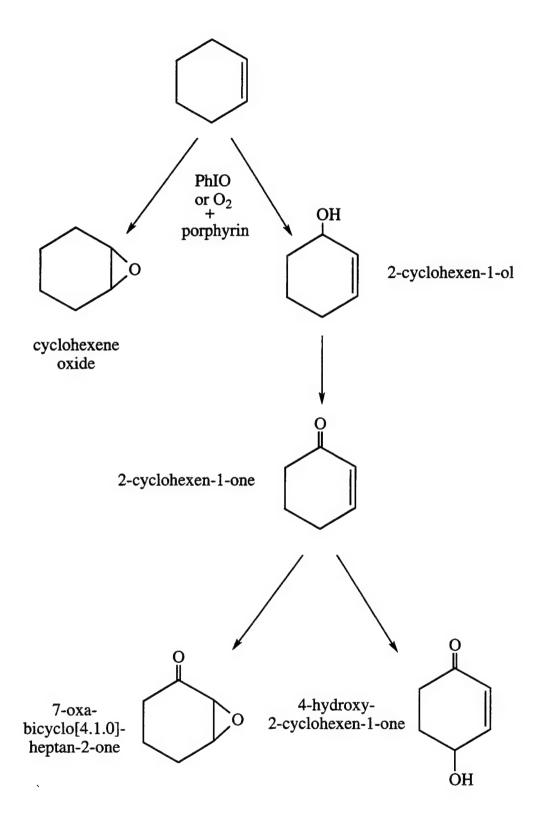
Figure 6.12 – Turnovers of cyclohexene observed in oxidation reactions with RuTFPPCl$_8$(CO) and either iodosobenzene (left) or dioxygen (right). PhIO data is after 4 hours, and the dioxygen results are at 24 hours (CH$_2$Cl$_2$) or 12 hours (SC CO$_2$) in the different solvents. Higher selectivity for epoxide formation is observed with PhIO in SC CO$_2$ relative to CH$_2$Cl$_2$. The dioxygen reactions are not as effective in the supercritical solvent.

Legend:
- ■ cyclohexene oxide
- ▦ 2-cyclohexen-1-ol
- ▧ 2-cyclohexen-1-one
- ◪ 7-oxa-bicylo[4.1.0]-heptan-2-one
- ▥ 4-hydroxy-2-cyclohexen-1-one
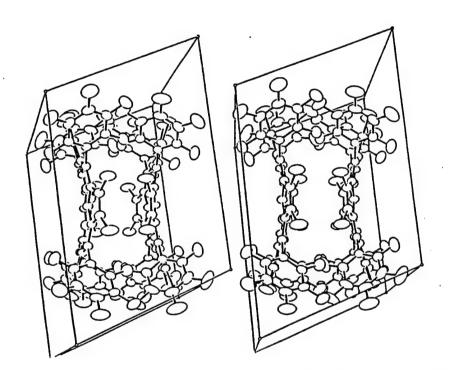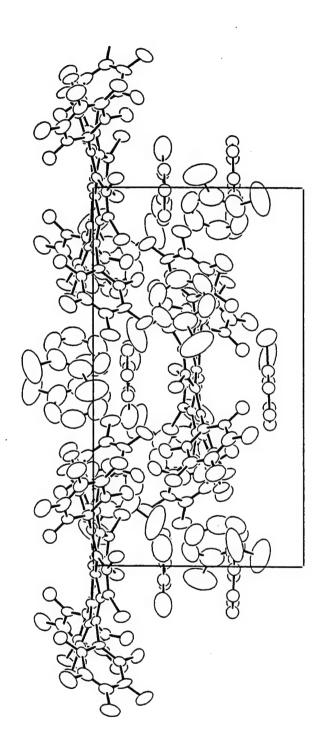
Figure 6.13 -- Partitioning mechanism to higher oxidation products.

cyclohexene

PhIO
or O_2
+
porphyrin

cyclohexene
oxide

OH

2-cyclohexen-1-ol

2-cyclohexen-1-one

7-oxa-
bicyclo[4.1.0]-
heptan-2-one

4-hydroxy-
2-cyclohexen-1-one

OH
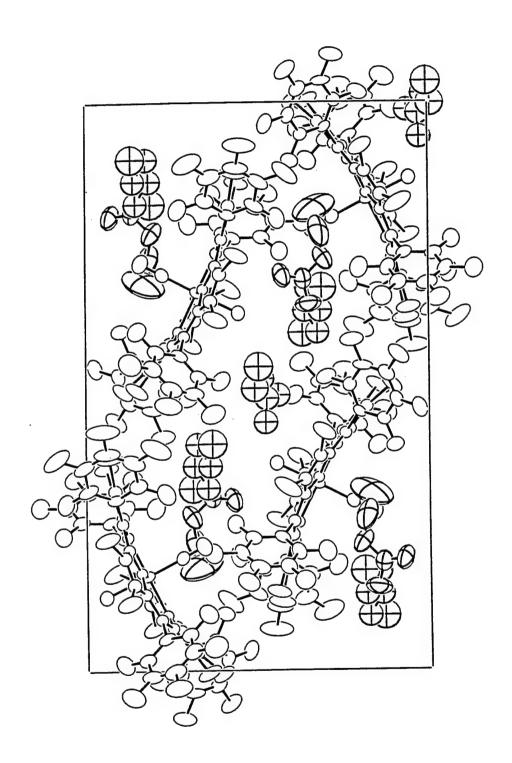
Appendix 2

Crystal Structure Data

Table 1. **Final Heavy Atom Parameters for**

Tetrakis(pentafluorophenyl)-β-octachloroporphyrin

x, y, z and $U_{eq}{}^a \times 10^4$

Atom	x	y	z	U_{eq}
Cl1	8772(1)	7676(1)	3695(1)	599(2)
Cl2	9105(1)	7909(1)	5768(1)	564(2)
Cl3	7030(1)	6297(1)	9358(1)	649(3)
Cl4	6863(1)	4203(1)	9784(1)	565(3)
Cl5	8296(1)	666(1)	7251(1)	551(2)
Cl6	8017(1)	388(1)	5189(1)	594(3)
Cl7	5875(1)	3260(1)	2544(1)	610(2)
Cl8	6089(1)	5349(1)	2107(1)	588(2)
N1	7751(2)	5801(2)	5404(2)	322(6)
N2	7639(2)	4666(2)	7079(2)	303(6)
N3	7448(2)	3089(2)	5970(2)	292(6)
N4	7218(2)	4335(2)	4383(2)	311(6)
C1	7855(3)	6171(2)	4534(2)	305(6)
C2	8351(3)	6968(2)	4569(2)	347(7)
C3	8477(3)	7076(2)	5450(2)	349(7)
C4	8058(3)	6354(2)	6001(2)	318(7)
C5	7890(3)	6276(2)	6972(2)	315(7)
C6	7600(3)	5516(2)	7474(2)	305(7)
C7	7306(3)	5446(2)	8484(2)	346(7)
C8	7231(3)	4562(2)	8666(2)	335(7)

Table 1. (Cont.)

Atom	x	y	z	U_{eq}
C9	7464(3)	4046(2)	7771(2)	295(7)
C10	7580(3)	3079(2)	7622(2)	285(6)
C11	7659(3)	2624(2)	6766(2)	287(6)
C12	7889(3)	1611(2)	6566(2)	308(7)
C13	7771(3)	1499(2)	5684(2)	318(7)
C14	7451(3)	2439(2)	5303(2)	278(6)
C15	7112(3)	2674(2)	4449(2)	298(7)
C16	6922(3)	3579(2)	4059(2)	310(6)
C17	6483(3)	3861(2)	3212(2)	349(7)
C18	6571(3)	4745(2)	3031(2)	350(7)
C19	7080(3)	5043(2)	3756(2)	304(7)
C20	7459(3)	5865(2)	3788(2)	299(7)
C21	7988(3)	7087(2)	7529(2)	313(7)
C22	6947(3)	7927(2)	7798(2)	356(7)
C23	6998(3)	8682(2)	8311(2)	417(9)
C24	8127(4)	8587(2)	8595(2)	454(9)
C25	9175(3)	7759(2)	8359(2)	444(8)
C26	9107(3)	7027(2)	7820(2)	390(8)
C31	7581(3)	2476(2)	8462(2)	287(6)
C32	8712(3)	2034(2)	8757(2)	346(7)

Table 1. (Cont.)

Atom	x	y	z	U_{eq}
C33	8719(3)	1485(2)	9522(2)	412(8)
C34	7567(4)	1361(2)	10009(2)	491(10)
C35	6431(3)	1784(2)	9738(2)	465(9)
C36	6446(3)	2343(2)	8980(2)	368(7)
C41	7026(3)	1869(2)	3882(2)	313(7)
C42	8108(3)	1325(2)	3209(2)	388(7)
C43	8109(4)	554(2)	2699(2)	516(9)
C44	7008(4)	292(2)	2873(3)	572(10)
C45	5909(4)	799(3)	3536(3)	573(9)
C46	5909(3)	1603(2)	4018(2)	426(8)
C51	7431(3)	6472(2)	2950(2)	306(6)
C52	8481(3)	6277(2)	2166(2)	387(8)
C53	8433(4)	6815(3)	1389(2)	478(9)
C54	7343(4)	7583(3)	1397(2)	488(9)
C55	6295(3)	7816(2)	2163(3)	454(9)
C56	6344(3)	7253(2)	2920(2)	357(7)
F22	5813(2)	8012(1)	7569(1)	587(5)
F23	5974(2)	9491(1)	8548(2)	679(6)
F24	8193(2)	9314(1)	9096(1)	721(6)
F25	10283(2)	7663(2)	8629(2)	740(6)

Table 1. (Cont.)

Atom	x	y	z	U_{eq}
F26	10183(2)	6251(1)	7549(2)	661(6)
F32	9855(2)	2125(1)	8267(1)	526(5)
F33	9839(2)	1063(1)	9778(1)	670(6)
F34	7552(2)	820(2)	10752(1)	833(7)
F35	5305(2)	1658(2)	10213(2)	825(7)
F36	5305(2)	2795(1)	8753(1)	560(5)
F42	9238(2)	1523(2)	3072(1)	628(6)
F43	9185(2)	56(2)	2043(2)	916(7)
F44	7005(3)	−470(2)	2384(2)	1022(8)
F45	4818(3)	549(2)	3707(2)	985(7)
F46	4808(2)	2121(2)	4628(2)	765(7)
F52	9591(2)	5562(1)	2157(1)	677(6)
F53	9461(2)	6597(2)	639(1)	827(7)
F54	7293(3)	8122(2)	650(2)	864(7)
F55	5208(2)	8568(1)	2179(2)	750(6)
F56	5271(2)	7458(1)	3637(1)	627(6)

^{a} $U_{eq} = \frac{1}{3} \sum_i \sum_j [U_{ij}(a_i^* a_j^*)(\vec{a}_i \cdot \vec{a}_j)]$

Table 2. Selected Distances and Angles for

Tetrakis(pentafluorophenyl)-β-octachloroporphyrin

	Distance(Å)		Distance(Å)
Cl1 –C2	1.706(3)	C4 –C5	1.400(4)
Cl2 –C3	1.705(3)	C5 –C6	1.404(4)
Cl3 –C7	1.708(3)	C6 –C7	1.449(4)
Cl4 –C8	1.708(3)	C7 –C8	1.341(4)
Cl5 –C12	1.702(3)	C8 –C9	1.453(4)
Cl6 –C13	1.706(3)	C9 –C10	1.396(4)
Cl7 –C17	1.708(3)	C10 –C11	1.402(4)
Cl8 –C18	1.706(3)	C11 –C12	1.445(4)
N1 –C1	1.372(4)	C12 –C13	1.350(4)
N1 –C4	1.372(4)	C13 –C14	1.446(4)
N2 –C6	1.366(4)	C14 –C15	1.399(4)
N2 –C9	1.370(4)	C15 –C16	1.407(4)
N3 –C11	1.373(4)	C16 –C17	1.448(4)
N3 –C14	1.377(4)	C17 –C18	1.346(4)
N4 –C16	1.373(4)	C18 –C19	1.450(4)
N4 –C19	1.369(4)	C19 –C20	1.400(4)
C1 –C2	1.446(4)		
C1 –C20	1.404(4)		
C2 –C3	1.350(4)		
C3 –C4	1.445(4)		

Table 2. (Cont.)

	Angle(°)			Angle(°)
C4 –N1 –C1	109.9(2)		C6 –C7 –Cl3	129.5(2)
C9 –N2 –C6	109.4(2)		C8 –C7 –Cl3	122.2(2)
C14 –N3 –C11	109.5(2)		C8 –C7 –C6	108.3(3)
C19 –N4 –C16	109.1(2)		C7 –C8 –Cl4	122.6(2)
C2 –C1 –N1	106.8(2)		C9 –C8 –Cl4	129.8(2)
C20 –C1 –N1	125.4(3)		C9 –C8 –C7	107.6(3)
C20 –C1 –C2	127.6(3)		C8 –C9 –N2	107.4(2)
C1 –C2 –Cl1	129.4(2)		C10 –C9 –N2	125.4(3)
C3 –C2 –Cl1	122.5(2)		C10 –C9 –C8	127.1(3)
C3 –C2 –C1	108.1(3)		C11 –C10 –C9	126.0(3)
C2 –C3 –Cl2	122.7(2)		C10 –C11 –N3	125.1(3)
C4 –C3 –Cl2	129.2(2)		C12 –C11 –N3	107.2(2)
C4 –C3 –C2	108.0(3)		C12 –C11 –C10	127.6(3)
C3 –C4 –N1	106.9(2)		C11 –C12 –Cl5	129.2(2)
C5 –C4 –N1	125.9(3)		C13 –C12 –Cl5	122.7(2)
C5 –C4 –C3	127.0(3)		C13 –C12 –C11	108.1(2)
C6 –C5 –C4	125.6(3)		C12 –C13 –Cl6	121.5(2)
C5 –C6 –N2	125.1(3)		C14 –C13 –Cl6	130.4(2)
C7 –C6 –N2	107.3(2)		C14 –C13 –C12	108.0(3)
C7 –C6 –C5	127.4(3)		C13 –C14 –N3	107.1(2)

Table 2. (Cont.)

Angle(°)

C15 –C14 –N3	125.5(2)
C15 –C14 –C13	127.3(3)
C16 –C15 –C14	125.8(3)
C15 –C16 –N4	125.5(3)
C17 –C16 –N4	107.5(2)
C17 –C16 –C15	126.9(3)
C16 –C17 –Cl7	129.1(2)
C18 –C17 –Cl7	122.9(2)
C18 –C17 –C16	107.9(3)
C17 –C18 –Cl8	122.2(2)
C19 –C18 –Cl8	130.0(2)
C19 –C18 –C17	107.8(3)
C18 –C19 –N4	107.6(2)
C20 –C19 –N4	125.3(3)
C20 –C19 –C18	127.0(3)
C19 –C20 –C1	125.6(3)

Table S1. Anisotropic Displacement Parameters for Tetrakis(pentafluorophenyl)-β-octachloroporphyrin

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl1	990(8)	710(6)	410(5)	−647(6)	−262(5)	235(4)
Cl2	906(7)	624(6)	459(5)	−589(5)	−259(5)	119(4)
Cl3	1245(9)	425(5)	309(5)	−384(5)	−93(5)	−55(4)
Cl4	1022(8)	439(5)	247(4)	−315(5)	−78(4)	41(4)
Cl5	979(7)	284(4)	484(5)	−179(4)	−401(5)	126(4)
Cl6	1110(8)	252(4)	520(5)	−199(5)	−417(5)	35(4)
Cl7	1028(8)	488(5)	657(6)	−422(5)	−616(6)	178(4)
Cl8	1017(8)	492(5)	554(6)	−402(5)	−552(5)	253(4)
N1	476(16)	288(13)	286(14)	−200(12)	−150(12)	53(11)
N2	421(15)	286(13)	235(13)	−146(11)	−102(12)	13(11)
N3	399(15)	245(13)	269(13)	−126(11)	−127(11)	41(11)
N4	459(16)	271(13)	275(14)	−164(12)	−166(12)	43(11)
C1	385(18)	312(16)	283(16)	−166(14)	−133(14)	53(13)
C2	443(19)	359(17)	320(17)	−226(15)	−118(15)	81(13)
C3	436(19)	323(16)	384(18)	−220(15)	−147(15)	52(14)
C4	408(18)	283(16)	327(17)	−171(14)	−134(14)	49(13)
C5	385(18)	282(16)	328(17)	−146(14)	−132(14)	21(13)
C6	364(18)	274(16)	307(16)	−118(13)	−118(14)	12(13)
C7	468(19)	310(17)	261(16)	−126(14)	−89(14)	−21(13)
C8	427(19)	333(17)	255(16)	−138(14)	−85(14)	40(13)
C9	369(18)	302(16)	236(15)	−129(13)	−93(13)	40(13)
C10	329(17)	293(16)	262(16)	−121(13)	−106(13)	65(12)
C11	301(16)	286(16)	296(16)	−111(13)	−98(13)	60(13)
C12	367(17)	250(15)	338(17)	−113(13)	−131(14)	82(13)
C13	382(18)	258(15)	344(17)	−117(13)	−129(14)	11(13)
C14	318(17)	250(15)	286(16)	−100(13)	−102(13)	12(12)
C15	327(17)	279(16)	311(16)	−122(13)	−91(13)	−2(13)
C16	393(18)	311(16)	287(16)	−159(14)	−135(14)	25(13)
C17	453(19)	343(17)	334(17)	−158(15)	−213(15)	23(13)
C18	451(19)	325(17)	346(17)	−152(15)	−200(15)	100(13)
C19	376(18)	302(16)	280(16)	−142(14)	−126(14)	49(13)
C20	326(17)	299(16)	286(16)	−108(13)	−99(13)	64(12)
C21	425(19)	281(16)	295(16)	−172(14)	−128(14)	44(13)
C22	386(19)	362(18)	404(18)	−200(15)	−150(15)	80(14)
C23	540(22)	253(17)	422(19)	−137(16)	−41(17)	10(14)
C24	740(26)	390(20)	363(19)	−338(19)	−166(18)	10(15)
C25	546(22)	522(22)	432(20)	−299(19)	−264(17)	94(16)
C26	484(21)	316(17)	391(18)	−123(16)	−158(16)	36(14)
C31	399(18)	260(15)	243(15)	−139(13)	−116(14)	42(12)

Table S1. (Cont.)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C32	411(20)	330(17)	319(17)	−135(15)	−112(15)	13(14)
C33	522(22)	367(18)	347(18)	−51(16)	−239(17)	36(14)
C34	745(27)	373(19)	293(18)	−116(18)	−116(18)	140(15)
C35	490(22)	441(20)	406(20)	−181(17)	29(17)	128(16)
C36	385(19)	330(17)	401(19)	−107(15)	−135(16)	76(14)
C41	413(19)	298(16)	300(16)	−157(14)	−169(15)	45(13)
C42	460(21)	385(18)	381(18)	−145(16)	−207(16)	2(15)
C43	599(24)	436(20)	461(21)	17(19)	−279(19)	−124(17)
C44	871(31)	346(20)	657(26)	−228(21)	−437(24)	−20(18)
C45	745(28)	633(25)	678(26)	−512(23)	−420(23)	217(21)
C46	450(21)	481(20)	416(19)	−219(17)	−145(17)	55(16)
C51	389(18)	301(16)	285(16)	−169(14)	−112(14)	45(13)
C52	387(19)	396(18)	395(19)	−131(16)	−123(16)	28(15)
C53	566(23)	618(23)	307(19)	−332(20)	−22(17)	37(17)
C54	789(28)	526(22)	377(20)	−421(21)	−299(20)	215(17)
C55	559(23)	300(18)	625(24)	−154(17)	−359(20)	105(16)
C56	381(19)	335(17)	376(18)	−122(15)	−124(16)	25(14)
F22	486(12)	505(12)	829(15)	−148(10)	−287(11)	16(10)
F23	746(15)	350(11)	807(15)	−90(11)	−59(12)	−71(10)
F24	1212(19)	508(12)	648(13)	−470(13)	−342(13)	−83(10)
F25	833(16)	822(15)	872(16)	−431(13)	−559(13)	86(12)
F26	543(13)	518(12)	906(16)	−45(10)	−317(12)	−74(11)
F32	403(11)	650(13)	584(12)	−227(10)	−160(10)	108(10)
F33	760(15)	639(13)	603(13)	−28(11)	−433(12)	82(10)
F34	1148(19)	766(15)	455(12)	−179(14)	−165(12)	367(11)
F35	685(15)	841(16)	814(16)	−298(13)	111(13)	347(13)
F36	402(11)	624(12)	681(13)	−178(10)	−181(10)	186(10)
F42	434(12)	861(15)	598(13)	−242(11)	−87(10)	−140(11)
F43	807(17)	874(17)	819(16)	178(14)	−324(14)	−470(14)
F44	1617(25)	521(14)	1228(21)	−413(15)	−803(19)	−154(13)
F45	1173(21)	1190(20)	1143(20)	−981(18)	−508(17)	282(16)
F46	526(14)	1098(18)	679(15)	−393(13)	21(12)	−121(13)
F52	472(12)	650(13)	701(14)	4(11)	−17(10)	13(11)
F53	941(17)	1098(18)	423(13)	−532(15)	142(12)	7(12)
F54	1436(22)	877(16)	590(14)	−641(16)	−494(14)	462(12)
F55	817(16)	459(12)	1065(18)	−88(11)	−575(14)	203(11)
F56	442(12)	663(13)	621(13)	−62(10)	−7(11)	5(10)

$U_{i,j}$ values have been multiplied by 10^4

The form of the displacement factor is:

$$\exp -2\pi^2(U_{11}h^2a^{*^2} + U_{22}k^2b^{*^2} + U_{33}\ell^2c^{*^2} + 2U_{12}hka^*b^* + 2U_{13}h\ell a^*c^* + 2U_{23}k\ell b^*c^*)$$

Table S2. Hydrogen Atom Parameters for
Tetrakis(pentafluorophenyl)-β-octachloroporphyrin

x, y and $z \times 10^4$

Atom	x	y	z	B
H1	7559(53)	5227(40)	5567(38)	3.0
H2	7773(55)	4537(41)	6517(41)	2.9
H3	7317(51)	3747(40)	5918(37)	2.8
H4	7414(55)	4351(40)	4900(40)	2.9

All atoms have a population factor of one-half.

Table S3. Complete Distances and Angles for

Tetrakis(pentafluorophenyl)-β-octachloroporphyrin

	Distance(Å)		Distance(Å)
Cl1 –C2	1.706(3)	C15 –C41	1.496(4)
Cl2 –C3	1.705(3)	C16 –C17	1.448(4)
Cl3 –C7	1.708(3)	C17 –C18	1.346(4)
Cl4 –C8	1.708(3)	C18 –C19	1.450(4)
Cl5 –C12	1.702(3)	C19 –C20	1.400(4)
Cl6 –C13	1.706(3)	C20 –C51	1.506(4)
Cl7 –C17	1.708(3)	C21 –C22	1.373(4)
Cl8 –C18	1.706(3)	C21 –C26	1.381(4)
N1 –C1	1.372(4)	C22 –C23	1.372(4)
N1 –C4	1.372(4)	C22 –F22	1.343(4)
N1 –H1	0.94(6)	C23 –C24	1.375(5)
N2 –C6	1.366(4)	C23 –F23	1.331(4)
N2 –C9	1.370(4)	C24 –C25	1.361(5)
N2 –H2	0.82(6)	C24 –F24	1.335(4)
N3 –C11	1.373(4)	C25 –C26	1.375(5)
N3 –C14	1.377(4)	C25 –F25	1.342(4)
N3 –H3	0.93(6)	C26 –F26	1.337(4)
N4 –C16	1.373(4)	C31 –C32	1.380(4)
N4 –C19	1.369(4)	C31 –C36	1.373(4)
N4 –H4	0.84(6)	C32 –C33	1.370(4)
C1 –C2	1.446(4)	C32 –F32	1.342(3)
C1 –C20	1.404(4)	C33 –C34	1.369(5)
C2 –C3	1.350(4)	C33 –F33	1.335(4)
C3 –C4	1.445(4)	C34 –C35	1.363(5)
C4 –C5	1.400(4)	C34 –F34	1.336(4)
C5 –C6	1.404(4)	C35 –C36	1.368(5)
C5 –C21	1.500(4)	C35 –F35	1.340(4)
C6 –C7	1.449(4)	C36 –F36	1.343(4)
C7 –C8	1.341(4)	C41 –C42	1.374(4)
C8 –C9	1.453(4)	C41 –C46	1.380(4)
C9 –C10	1.396(4)	C42 –C43	1.365(5)
C10 –C11	1.402(4)	C42 –F42	1.341(4)
C10 –C31	1.503(4)	C43 –C44	1.359(5)
C11 –C12	1.445(4)	C43 –F43	1.339(4)
C12 –C13	1.350(4)	C44 –C45	1.362(6)
C13 –C14	1.446(4)	C44 –F44	1.338(5)
C14 –C15	1.399(4)	C45 –C46	1.385(5)
C15 –C16	1.407(4)	C45 –F45	1.337(5)

Table S3. (Cont.)

	Distance(Å)		Angle(°)
C46 –F46	1.329(4)	C4 –N1 –C1	109.9(2)
C51 –C52	1.382(4)	H1 –N1 –C1	125.9(35)
C51 –C56	1.377(4)	H1 –N1 –C4	124.1(35)
C52 –C53	1.377(5)	C9 –N2 –C6	109.4(2)
C52 –F52	1.331(4)	H2 –N2 –C6	125.7(42)
C53 –C54	1.357(5)	H2 –N2 –C9	124.9(42)
C53 –F53	1.336(4)	C14 –N3 –C11	109.5(2)
C54 –C55	1.362(5)	H3 –N3 –C11	123.1(35)
C54 –F54	1.341(4)	H3 –N3 –C14	127.4(35)
C55 –C56	1.373(5)	C19 –N4 –C16	109.1(2)
C55 –F55	1.341(4)	H4 –N4 –C16	123.6(40)
C56 –F56	1.337(4)	H4 –N4 –C19	127.3(41)
		C2 –C1 –N1	106.8(2)
		C20 –C1 –N1	125.4(3)
		C20 –C1 –C2	127.6(3)
		C1 –C2 –Cl1	129.4(2)
		C3 –C2 –Cl1	122.5(2)
		C3 –C2 –C1	108.1(3)
		C2 –C3 –Cl2	122.7(2)
		C4 –C3 –Cl2	129.2(2)
		C4 –C3 –C2	108.0(3)
		C3 –C4 –N1	106.9(2)
		C5 –C4 –N1	125.9(3)
		C5 –C4 –C3	127.0(3)
		C6 –C5 –C4	125.6(3)
		C21 –C5 –C4	117.3(2)
		C21 –C5 –C6	117.1(2)
		C5 –C6 –N2	125.1(3)
		C7 –C6 –N2	107.3(2)
		C7 –C6 –C5	127.4(3)
		C6 –C7 –Cl3	129.5(2)
		C8 –C7 –Cl3	122.2(2)
		C8 –C7 –C6	108.3(3)
		C7 –C8 –Cl4	122.6(2)
		C9 –C8 –Cl4	129.8(2)
		C9 –C8 –C7	107.6(3)
		C8 –C9 –N2	107.4(2)
		C10 –C9 –N2	125.4(3)

Table S3. (Cont.)

	Angle(°)			Angle(°)
C10 –C9 –C8	127.1(3)		F22 –C22 –C21	118.9(3)
C11 –C10 –C9	126.0(3)		F22 –C22 –C23	118.0(3)
C31 –C10 –C9	117.0(2)		C24 –C23 –C22	118.8(3)
C31 –C10 –C11	116.9(2)		F23 –C23 –C22	121.3(3)
C10 –C11 –N3	125.1(3)		F23 –C23 –C24	119.9(3)
C12 –C11 –N3	107.2(2)		C25 –C24 –C23	120.1(3)
C12 –C11 –C10	127.6(3)		F24 –C24 –C23	119.6(3)
C11 –C12 –Cl5	129.2(2)		F24 –C24 –C25	120.3(3)
C13 –C12 –Cl5	122.7(2)		C26 –C25 –C24	119.7(3)
C13 –C12 –C11	108.1(2)		F25 –C25 –C24	120.5(3)
C12 –C13 –Cl6	121.5(2)		F25 –C25 –C26	119.8(3)
C14 –C13 –Cl6	130.4(2)		C25 –C26 –C21	122.2(3)
C14 –C13 –C12	108.0(3)		F26 –C26 –C21	119.7(3)
C13 –C14 –N3	107.1(2)		F26 –C26 –C25	118.1(3)
C15 –C14 –N3	125.5(2)		C32 –C31 –C10	122.1(3)
C15 –C14 –C13	127.3(3)		C36 –C31 –C10	121.4(3)
C16 –C15 –C14	125.8(3)		C36 –C31 –C32	116.5(3)
C41 –C15 –C14	116.5(2)		C33 –C32 –C31	122.4(3)
C41 –C15 –C16	117.7(2)		F32 –C32 –C31	119.1(3)
C15 –C16 –N4	125.5(3)		F32 –C32 –C33	118.5(3)
C17 –C16 –N4	107.5(2)		C34 –C33 –C32	119.0(3)
C17 –C16 –C15	126.9(3)		F33 –C33 –C32	120.4(3)
C16 –C17 –Cl7	129.1(2)		F33 –C33 –C34	120.6(3)
C18 –C17 –Cl7	122.9(2)		C35 –C34 –C33	120.3(3)
C18 –C17 –C16	107.9(3)		F34 –C34 –C33	120.1(3)
C17 –C18 –Cl8	122.2(2)		F34 –C34 –C35	119.6(3)
C19 –C18 –Cl8	130.0(2)		C36 –C35 –C34	119.6(3)
C19 –C18 –C17	107.8(3)		F35 –C35 –C34	120.2(3)
C18 –C19 –N4	107.6(2)		F35 –C35 –C36	120.2(3)
C20 –C19 –N4	125.3(3)		C35 –C36 –C31	122.2(3)
C20 –C19 –C18	127.0(3)		F36 –C36 –C31	119.0(3)
C19 –C20 –C1	125.6(3)		F36 –C36 –C35	118.7(3)
C51 –C20 –C1	117.4(2)		C42 –C41 –C15	120.2(3)
C51 –C20 –C19	117.0(2)		C46 –C41 –C15	123.3(3)
C22 –C21 –C5	121.4(3)		C46 –C41 –C42	116.5(3)
C26 –C21 –C5	122.5(3)		C43 –C42 –C41	122.9(3)
C26 –C21 –C22	116.1(3)		F42 –C42 –C41	119.2(3)
C23 –C22 –C21	123.1(3)		F42 –C42 –C43	117.8(3)

Table S3. (Cont.)

Angle(°)

C44 –C43 –C42	119.1(3)
F43 –C43 –C42	120.6(3)
F43 –C43 –C44	120.3(3)
C45 –C44 –C43	120.6(4)
F44 –C44 –C43	119.6(3)
F44 –C44 –C45	119.9(4)
C46 –C45 –C44	119.4(4)
F45 –C45 –C44	121.0(4)
F45 –C45 –C46	119.6(3)
C45 –C46 –C41	121.4(3)
F46 –C46 –C41	119.8(3)
F46 –C46 –C45	118.8(3)
C52 –C51 –C20	122.2(3)
C56 –C51 –C20	121.6(3)
C56 –C51 –C52	116.2(3)
C53 –C52 –C51	122.0(3)
F52 –C52 –C51	119.9(3)
F52 –C52 –C53	118.1(3)
C54 –C53 –C52	119.5(3)
F53 –C53 –C52	120.3(3)
F53 –C53 –C54	120.1(3)
C55 –C54 –C53	120.5(3)
F54 –C54 –C53	120.1(3)
F54 –C54 –C55	119.4(3)
C56 –C55 –C54	119.2(3)
F55 –C55 –C54	121.2(3)
F55 –C55 –C56	119.6(3)
C55 –C56 –C51	122.6(3)
F56 –C56 –C51	119.4(3)
F56 –C56 –C55	118.1(3)

Table S4.   Observed and Calculated Structure Factors for

Tetrakis(pentafluorophenyl)-β-octachloroporphyrin

The columns contain, in order, ℓ, $10F_{obs}$, $10F_{calc}$ and $10\sigma F_{obs}$. A minus sign preceding F_{obs} indicates that F_{obs}^2 is negative.

Tetrakis(pentafluorophenyl)-beta-octachloroporphyrin   Page   1

```
 -10  1  1            6  117  115  5        5   47    8  9        1  251  257  4
                                            6   99  105  6        2  142  145  4
  1  182  227  5     -8  4  1               7  102  111  6        3   94   78  5
  2  -14    2 16                                                  4  131  122  4
  3   42   47  8      1  132  125  5        -7  6  1               5   10   10 19
                      2   48   39  8                              6   51   34  8
 -10  2  1            3  220  237  4        1  120  118  5        7   20   35 15
                      4  203  203  5        2   42   17  9        8   37   48 11
  1   39   41 10      5   79   61  6        3   96   87  5
  2   16   28 18                            4  208  200  5       -6  6  1
                     -8  5  1               5  162  160  5
 -10  3  1                                  6  116  109  5        1   36   17  9
                      1   60   48  7                              2  133  139  4
  1   80   63  6      2   53   29  8        -7  7  1               3   93   93  5
                      3  188  189  5                              4  285  271  4
 -9  1  1             4   65   62  7        1   79   87  6        5   46   27  9
                                            2  232  240  4        6  125  139  5
  1  117  104  5     -8  6  1               3   98   98  6        7   73   72  7
  2   56   31  7                            4   61   58  7
  3  142  132  5      1  129  128  5                             -6  7  1
  4  -21    8 14      2  149  149  5        -7  8  1
  5   11   17 21      3   76   57  7                              1  249  261  4
  6   73   42  7                            1  -21    7 14        2   33   50 10
                     -8  7  1               2   61   88  7        3  -29    1  9
 -9  2  1                                   3   58   77  7        4  237  245  4
                      1  115  117  5                              5  121  117  5
  1   50   31  7                            -6  1  1               6   46   43  7
  2   23   46 13     -7  1  1
  3   60   65  7                            1  343  362  4       -6  8  1
  4   61   67  8      1   26   17 10        2  347  349  4
  5  156  151  5      2   46   59  7        3  199  185  4        1  113  113  5
                      3   84   76  5        4  184  183  4        2   75   92  6
 -9  3  1             4   33    7  9        5   66   44  6        3   31   37 11
                      5  145  141  4        6   73   68  6        4   43   39  9
  1   84   81  6      6  137  137  5        7  209  213  4        5   53   21  8
  2   54   47  8      7   54   75  8        8  121  112  5
  3   71   71  7      8   73   81  7        9   37   23 11       -6  9  1
  4   60   77  8      9  -38   10 10       10  119  112  5
                                                                 1  105  124  5
 -9  4  1            -7  2  1               -6  2  1              2   57   61  8
                                                                 3  -43    6  8
  1   65   88  7      1  111  108  4        1  264  272  4
  2   36   29 11      2   42   27  8        2  106  120  4       -6 10  1
  3   38   17 11      3  284  296  4        3  206  212  4
                      4   50   51  6        4   99  107  4        1   80   58  6
 -9  5  1             5  141  139  4        5   39   24  8
                      6   94  104  5        6  264  268  4       -5  1  1
  1  110   97  5      7  161  140  5        7   76   61  6
                      8   67   42  7        8   78   69  6        1  159  157  3
 -8  1  1             9   29   11 13        9  257  257  5        2  278  272  3
                                           10   47   58  9        3  521  517  5
  1  931  921  8     -7  3  1                                     4  539  534  5
  2  278  278  4                            -6  3  1              5   73   55  5
  3   55   47  7      1  192  194  4                              6  134  126  4
  4  119  122  5      2   97   92  5        1  200  199  4        7  287  277  4
  5   40   24  8      3  105  112  5        2  193  192  4        8  -12    3 17
  6  152  155  5      4  192  190  4        3  125  125  4        9  328  328  5
  7   98   97  6      5   38   29  9        4  233  236  4       10   68   71  6
  8    5   15 26      6  170  182  5        5  111  132  5       11   84   75  6
                      7   31    5 11        6  166  177  4       12  107  100  6
 -8  2  1             8  116  110  5        7  179  176  4
                                            8   25   34 13       -5  2  1
  1  116   86  4     -7  4  1               9  174  160  5
  2  206  201  4                           10   14   28 20        1  396  399  4
  3  139  122  4      1  116  126  4                              2  135  130  3
  4   65   59  7      2  162  180  4        -6  4  1              3  447  450  5
  5   12   16 19      3   50   36  8                              4  230  228  4
  6  196  192  5      4  198  208  4        1   50   26  6        5   41   32  7
  7  130  129  5      5  161  162  4        2   59   17  5        6  289  282  4
                      6  158  161  5        3  151  148  4        7   32   33 10
 -8  3  1             7   53   56  8        4   50   41  5        8  248  248  4
                                            5  221  222  4        9  136  129  5
  1  288  284  4     -7  5  1               6   40   27  9       10    8   27 22
  2  261  276  4                            7   84   74  6       11   71   71  7
  3  174  172  4      1   39   11  9        8  136  154  5
  4  100   85  5      2  189  187  4        9   46   29  8       -5  3  1
  5   68   57  7      3  143  158  4
                      4   70   53  6        -6  5  1
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Tetrakis(pentafluorophenyl)-beta-octachloroporphyrin   Page   2

```
 1  432  441   4        6   94  100   6        3   27    0   9         1  423  423   4
 2   43   35   6                                4  415  436   4         2  883  872   7
 3   84   87   4       -5  10   1               5  205  209   4         3  660  632   6
 4  230  227   4                                6   77   83   5         4   54    7   5
 5  229  225   4        1  110  124   5         7  160  158   4         5 1223 1209  10
 6  245  240   4        2   75   72   6         8  167  170   4         6   95   94   4
 7  110  107   5        3  -14   43  18         9  -21    5  13         7  161  164   4
 8   75   69   6        4   80   81   6        10  108   94   5         8  120  130   4
 9   60   71   7                               11   37   11  11         9  180  177   4
10   74   76   7       -5  11   1                                      10  113  111   5
11   56   65   8                               -4   6   1              11   26   49  13
                       1   53   51   7                                12  -55   14   6
-5   4   1             2   66   64   7          1  187  183   3        13  207  207   5
                                                2  354  350   4
 1  208  207   3      -4   1   1                3   64   48   5        -3   2   1
 2  113  124   4                                4   95   87   4
 3   68   52   5       1  522  509   5          5   99  107   5         1  533  533   5
 4  380  367   4       2  359  347   4          6  314  311   4         2  254  255   3
 5   46    0   7       3   63   59   4          7   58   66   7         3  493  504   4
 6   16   21  14       4   98  105   4          8  -20    8  14         4  401  399   4
 7   52   48   6       5  211  207   3          9  125  113   5         5  170  142   3
 8  -39   16   8       6   89   88   4         10   81   63   6         6   78   64   4
 9   30   51  12       7  332  328   4                                  7   44   40   7
10  -24   12  14       8  139  134   4         -4   7   1               8  141  160   4
                       9  272  279   4                                  9  200  194   4
-5   5   1            10  155  157   4          1   84   80   5        10  379  378   5
                      11  183  171   5          2   78   92   5        11  124  123   5
 1   79   73   4      12   70   79   7          3   67   70   5        12  161  153   5
 2  313  311   4      13  -16   11  18          4  269  272   4        13   83   83   6
 3  419  415   5                                5  151  154   4
 4  179  179   4      -4   2   1                6   71   70   6        -3   3   1
 5  245  248   4                                7  130  132   5
 6   36   52  10       1  977  994   8          8  326  319   5         1  791  792   7
 7   29   47  12       2  430  446   4          9  133  130   5         2   55   53   4
 8    3   24  24       3  352  356   4                                  3  188  183   3
 9   92   92   6       4  165  156   3         -4   8   1               4  159  161   3
10   71   72   7       5  151  155   3                                  5  835  827   7
                       6  175  168   4          1  162  172   4         6  -28    4   8
-5   6   1             7  336  334   4          2  129  131   4         7   20   13  12
                       8  208  194   4          3   31   24  10         8  -37    6   7
 1  249  242   4       9  150  150   4          4   87   96   5         9  266  259   4
 2  134  136   4      10  179  177   4          5   83   85   6        10  327  314   5
 3  331  332   4      11   88   92   6          6  168  157   4        11  145  138   5
 4   80   84   5      12  -30   27  12          7   59   62   7        12  214  207   5
 5   38   22   8                                8  165  167   5        13  192  196   5
 6   44   16   9      -4   3   1
 7  123  134   5                               -4   9   1              -3   4   1
 8   16   10  17       1  591  597   5
 9   86   86   6       2  353  360   4          1  272  265   4         1  137  135   3
                       3   58   33   5          2  178  168   4         2  171  166   3
-5   7   1             4  306  304   4          3   -2   40  25         3   70   73   4
                       5  335  330   4          4  189  185   4         4   61   51   5
 1   24   31  11       6  301  307   4          5  188  188   4         5  247  237   3
 2  -22    1  11       7  369  365   4          6  166  178   5         6  125  129   4
 3    3    0  22       8  136  138   4          7  168  183   5         7  130  143   4
 4   66   61   6       9  125  126   5                                  8   90   84   5
 5   53   49   8      10  -42   33   8         -4  10   1               9  309  313   4
 6  150  155   5      11  112  120   5                                 10  133  118   5
 7  142  141   5      12   29   25  13          1   41   38   9        11  336  331   5
 8   62   54   8                                2   50   16   8        12  142  127   5
                      -4   4   1                3   96   83   5
-5   8   1                                      4  106   94   5        -3   5   1
                       1  167  166   3          5  232  245   5
 1  -23   14  12       2  191  209   3          6   38   35  10         1  527  527   5
 2  -30    2  10       3   94   82   4                                  2  197  190   3
 3   57   72   7       4   80   78   4         -4  11   1               3   57   65   5
 4  108  107   5       5  427  432   5                                  4   45   37   5
 5   80   93   6       6  139  145   4          1   18    4  16         5  154  161   4
 6   10    8  21       7   33   30   9          2  183  167   5         6   68   73   5
 7  107  115   6       8  146  139   4          3   88   81   6         7  121  128   4
                       9   54   51   8          4   92   96   6         8   39   38   7
-5   9   1            10   17    1  16                                  9  164  154   4
                      11  -39    1   9         -4  12   1              10   70   52   7
 1   99  103   5                                                      11  200  196   5
 2  -40   23   8      -4   5   1                1   57   62   7        12   51   42   8
 3  116  116   5                                2   95   88   6
 4  -28   31  12       1  615  619   6                                 -3   6   1
 5  145  131   5       2   58   67   5         -3   1   1
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Tetrakis(pentafluorophenyl)-beta-octachloroporphyrin　　　　　　Page　3

1	713	718	6		**-3**	**13**	**1**		6	297	291	4		1	108	120	5
2	159	167	3						7	51	74	6		2	67	64	6
3	84	68	4		1	207	206	5		8	210	214	4		3	63	50	7
4	234	232	4						9	96	88	5		4	330	338	5
5	410	400	4		**-2**	**1**	**1**		10	57	64	7		5	226	220	4
6	151	153	4						11	66	79	7		6	44	15	9
7	72	73	6		1	1250	1234	10		12	232	233	5		7	158	138	5
8	170	187	4		2	1459	1455	10		13	21	7	16		8	279	260	5
9	249	243	4		3	1047	1051	9										
10	135	120	5		4	142	139	3		**-2**	**6**	**1**			**-2**	**12**	**1**
11	157	147	5		5	977	977	8										
					6	309	320	4		1	307	306	3		1	145	150	4
-3	**7**	**1**			7	399	399	4		2	83	78	4		2	146	145	5
					8	109	104	4		3	552	546	5		3	89	104	6
1	388	375	4		9	69	81	5		4	448	450	4		4	91	86	6
2	108	106	4		10	316	307	4		5	57	53	5		5	42	34	10
3	-12	5	15		11	81	108	6		6	300	298	4		6	50	65	9
4	230	230	4		12	49	81	8		7	143	142	4					
5	59	52	6		13	28	49	13		8	40	21	8		**-2**	**13**	**1**
6	231	230	4		14	157	162	5		9	47	43	8					
7	87	78	5							10	135	133	5		1	82	80	6
8	139	133	5		**-2**	**2**	**1**		11	106	114	5		2	44	27	9
9	54	47	8							12	11	4	21		3	101	83	6
10	32	51	12		1	238	219	3							4	241	222	5
11	66	68	7		2	574	581	5		**-2**	**7**	**1**					
					3	498	504	4							**-1**	**1**	**1**
-3	**8**	**1**			4	362	372	4		1	46	38	6					
					5	245	255	3		2	92	87	4		1	380	367	3
1	177	179	4		6	52	36	5		3	146	142	3		2	729	715	6
2	108	102	4		7	564	576	5		4	181	181	3		3	186	190	2
3	208	219	4		8	380	383	4		5	230	227	4		4	422	432	4
4	299	307	4		9	226	233	4		6	232	230	4		5	41	0	4
5	281	274	4		10	-11	11	18		7	205	211	4		6	163	163	3
6	73	60	6		11	242	228	4		8	248	251	4		7	53	86	5
7	50	50	6		12	146	143	5		9	136	116	5		8	454	465	5
8	193	181	4		13	75	71	7		10	101	107	5		9	53	52	6
9	41	67	9		14	222	216	5		11	207	191	5		10	430	433	5
10	-50	11	7												11	59	58	6
					-2	**3**	**1**		**-2**	**8**	**1**			12	144	139	4
-3	**9**	**1**												13	-46	6	7
					1	679	679	6		1	-21	27	10		14	90	96	6
1	283	265	4		2	61	51	4		2	66	72	5		15	107	107	6
2	173	169	4		3	106	115	3		3	119	112	4					
3	167	168	4		4	85	93	3		4	260	261	4		**-1**	**2**	**1**
4	183	197	4		5	303	298	3		5	67	54	5					
5	203	192	4		6	185	180	3		6	449	433	5		1	122	125	2
6	-11	30	19		7	76	70	4		7	30	12	11		2	425	408	4
7	66	65	7		8	40	37	7		8	400	404	5		3	152	138	2
8	115	107	5		9	130	141	4		9	219	221	4		4	783	795	7
9	104	108	6		10	77	84	6		10	56	49	8		5	12	4	12
					11	177	181	4		11	90	80	6		6	399	387	4
-3	**10**	**1**			12	151	152	5							7	95	105	4
					13	194	191	5		**-2**	**9**	**1**		8	803	798	7
1	251	250	4												9	927	926	8
2	107	107	5		**-2**	**4**	**1**		1	149	147	4		10	139	134	4
3	310	307	4							2	71	74	5		11	280	289	4
4	159	132	4		1	98	99	3		3	35	44	8		12	307	295	4
5	130	116	5		2	81	94	3		4	43	14	8		13	70	87	7
6	84	77	6		3	193	196	3		5	44	21	8		14	91	92	6
7	14	12	18		4	162	166	3		6	87	87	5					
8	65	35	7		5	428	429	4		7	166	153	4		**-1**	**3**	**1**
					6	209	204	3		8	157	155	5					
-3	**11**	**1**			7	38	44	7		9	70	67	7		1	446	436	4
					8	153	159	4		10	139	133	5		2	207	212	2
1	189	184	4		9	40	48	8							3	214	212	3
2	203	199	4		10	-32	41	10		**-2**	**10**	**1**		4	378	385	4
3	34	27	9		11	-33	24	10							5	120	113	3
4	58	33	7		12	-40	17	9		1	28	37	9		6	31	21	7
5	32	35	11		13	35	24	12		2	101	103	5		7	626	617	7
6	129	126	5							3	151	152	4		8	193	194	3
					-2	**5**	**1**		4	173	167	4		9	55	54	6
-3	**12**	**1**							5	367	370	5		10	139	142	4
					1	503	513	5		6	138	125	5		11	-36	16	9
1	99	88	5		2	287	286	3		7	243	246	4		12	318	323	5
2	205	206	5		3	285	291	3		8	-27	7	12		13	200	202	5
3	101	94	5		4	497	511	5		9	157	161	5		14	201	198	5
4	170	157	5		5	223	223	3										
										-2	**11**	**1**						

Tetrakis(pentafluorophenyl)-beta-octachloroporphyrin

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-1  4  1              -1  9  1          13  324  337  5    -10  639  635   6
 1  595  605   5                        14  221  215  5     -9  408  423   4
 2  307  302   3       1  143  153  4   15   72   64  7     -8   -6   29  17
 3   -9    5  13       2  111  101  4                       -7  341  346   4
 4  405  405   4       3  466  467  5    0   1   1          -6  885  853   8
 5  315  326   3       4  382  386  4                       -5 1988 2009  17
 6  172  164   3       5  416  410  5  -15  106  102  6     -4 1298 1311  11
 7  290  283   4       6   11    8 16  -14   55   42  6     -3  899  891   7
 8   37   25   8       7   22   45 13  -13  -20    8 14     -2  281  283   3
 9  216  210   4       8  169  165  4  -12   81   89  6     -1   58   67   3
10  156  165   4       9  172  171  4  -11  239  232  4      0  352  343   3
11   95   87   5      10   25   43 14  -10  137  136  4      1  971  955   8
12   30   47  11      11   74   72  7   -9  596  602  6      2  319  305   3
13  215  207   5                        -8  347  351  4      3 1286 1292  11
14   84   82   7      -1  10  1          -7  220  203  3      4  323  339   3
                                        -6  151  154  3      5  429  431   4
-1  5  1              1  -19   24 12    -5  216  219  3      6  356  355   4
                     2  248  251  4    -4  606  602  5      7  117  112   3
 1  369  368   4     3  401  399  5    -3  214  204  2      8  209  217   3
 2  990 1033   8     4  422  415  5    -2  201  208  2      9  117  117   4
 3  362  379   4     5  374  368  5    -1   52   14  3     10  265  259   4
 4  597  620   5     6  193  179  4     1  193  204  2     11  356  357   4
 5  765  764   7     7   56   43  7     2  869  869  7     12  287  281   4
 6  295  295   4     8   64   49  7     3  289  265  3     13  117  120   5
 7  144  144   4     9  -33    7 10     4  200  199  2     14  -27   39  12
 8  140  130   4    10   89   85  6     5 1108 1103  9     15  351  352   5
 9  292  284   4                        6  798  798  7
10  -15   37  16     -1  11  1          7  242  247  3      0   4   1
11   17   26  14                        8   28   46  8
12   77   92   6     1  -42    4  7     9   91   83  4    -15  126  132   5
13   66   85   7     2  100   96  5    10  -37    3  7    -14  201  216   5
                     3   36   28  8    11  638  640  6    -13  166  165   5
-1  6  1            4  631  627  6    12  364  365  5    -12   93  100   5
                     5   47    7  7    13  388  392  5    -11  199  203   4
 1  214  227   3     6  177  175  4    14   69   66  7    -10  -28    8   9
 2  189  192   3     7  -35    1  9    15  115  132  5     -9   86   90   4
 3  654  648   6     8   41   20 10                        -8   57   63   5
 4  584  592   5     9  160  148  5     0   2   1          -7  116  114   3
 5  331  328   4                                           -6 1333 1332  11
 6   26   10   9     -1  12  1        -15  230  221  5     -5  338  331   3
 7   87   79   4                      -14  336  336  5     -4  274  269   3
 8  674  675   6     1   -6    5 22  -13   93  101  5     -3 1184 1214  10
 9  204  192   4     2  216  211  4  -12  101  120  5     -2  195  205   2
10  116  117   5     3   58   34  6  -11  436  426  5     -1  422  424   4
11  227  232   4     4   75   83  6  -10  697  707  6      0  230  230   2
12  156  148   5     5  125  128  5   -9  229  240  4      1 1080 1093   9
13  117  118   6     6  -35   19 10   -8   49   42  6      2 1332 1331  11
                     7   74   82  7   -7  213  199  3      3 1088 1077   9
-1  7  1                                -6  309  303  3      4  901  919   8
                     -1  13  1        -5 1001 1012  8      5  220  234   3
 1  640  618   6                      -4  754  770  6      6  521  521   5
 2  163  161   3     1  107  116  5   -3  655  633  5      7   66   68   4
 3  249  241   3     2  133  123  5   -2  225  236  2      8  584  586   5
 4  107  102   4     3   55   60  8   -1  469  482  4      9   44   54   7
 5   51   56   6     4   36   32  8    0 1133 1209  9     10   76   82   5
 6  138  138   4     5   65   67  7    1   66   47  3     11   90   72   5
 7  359  354   4     6   56   60  8    2  623  615  5     12  437  421   5
 8   91   56   5                        3  238  245  2     13  -19    9  15
 9  798  785   7     -1  14  1        4 1115 1130  5     14   48   58   9
10   33   33  11                      5  453  464  4
11   74   80   6     1   60   58  7    6  124  133  3      0   5   1
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 1  297  290   4                      11  202  216  4    -12   90   88   5
 2   71   78   4     2 1011 1037  8   12   96   93  5    -11  577  563   6
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 5   98  100   4     5  491  484  4   15   91  105  6     -8  259  256   4
 6   16    3  14     6  580  571  5                        -7  -26    6   8
 7  196  196   4     7  104   80  3    0   3   1          -6  128  129   3
 8  178  171   4     8  177  198  3                        -5  603  570   5
 9  260  259   4     9  -20   12 11  -15   50   43  9     -4  206  199   3
10  182  175   4    10  273  268  4  -14   55   78  8     -3  327  326   3
11  162  158   5    11  139  133  4  -13  -41   30  8     -2  762  774   6
12  193  175   5    12  278  270  4  -12  120  137  5     -1 1048 1058   9
                                      -11  299  306  4      0  715  727   6
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  1  770  766   6      -13   95   98   6       7   75   86   6      -3   73   73   6
  2  202  200   3      -12  -26   38  11       8   65   69   7      -2   80   88   6
  3  660  687   6      -11  122  129   5       9  250  252   4      -1   86   96   6
  4  278  279   3      -10  -38   17   8      10  -38   12   9       0  126  121   5
  5  389  409   4       -9   67   84   6      11   54   68   8       1   42   30   9
  6  284  289   3       -8  258  257   4                             2   50   47   8
  7  230  231   3       -7   88   84   4      0  11  1               3  171  160   5
  8  102  111   4       -6  526  531   5                             4  250  236   5
  9  227  219   4       -5  358  359   4     -11  196  191   5       5   24   31  14
 10   79   92   5       -4  494  496   5     -10  107  115   5
 11  231  229   4       -3   85   90   4      -9  -30   13  11      0  15  1
 12  209  216   4       -2  215  218   3      -8  174  188   4
 13  110  103   5       -1   29   38   7      -7  -27   39  11      -3  124  122   5
 14   25   50  14        0  417  426   4      -6  195  195   4      -2  391  378   5
                         1   15   27  12      -5   31   52  10      -1   50   67   9
 0  6  1                 2   55   44   5      -4  148  149   4       0  -49   19   7
                         3  425  416   4      -3   38   48   8       1  141  133   5
-14  166  161   5        4  466  472   5      -2  229  235   4
-13  134  133   5        5  293  290   4      -1  395  401   4      1 -14  1
-12  -14   23  14        6  379  369   4       0  245  249   4
-11  339  339   4        7  263  254   4       1   15   35  13       0  249  238   5
-10  529  530   5        8  331  332   4       2   71   71   5       1   25   27  13
 -9  455  446   5        9  101  104   5       3  280  287   4       2  108  112   5
 -8   37   76   7       10  139  125   5       4  249  245   4       3  -34   25   9
 -7  287  289   4       11  149  154   5       5  133  122   4       4   91   91   6
 -6   60   50   5       12   94   80   6       6  258  256   4       5  147  130   5
 -5  300  293   3                              7  128  136   5       6  195  188   5
 -4  360  361   4       0  9  1                8  370  348   5
 -3  435  419   4                              9   49   14   7      1 -13  1
 -2  236  215   3      -13  128  140   5      10   56   37   8
 -1  514  513   5      -12   58   75   8                             0  183  184   4
  0  348  345   3      -11  -24   30  13      0  12  1               1  214  220   4
  1  473  484   4      -10  -44   11   7                             2  143  150   5
  2  302  316   3       -9   31   64  10     -10  235  229   5       3  178  166   4
  3  219  230   3       -8  659  667   6      -9   58   78   7       4  214  215   4
  4  220  233   3       -7   92   90   5      -8  116  121   5       5  158  137   5
  5   50   18   5       -6   40   22   7      -7  133  138   5       6  157  147   5
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  7   50   56   6       -4  319  324   4      -5  215  218   4       8   87   95   6
  8  365  378   4       -3  254  253   4      -4  404  406   5
  9  165  153   4       -2   83   90   4      -3  416  420   5      1 -12  1
 10   73   84   5       -1   27    6   9      -2  -24   38  11
 11  239  238   4        0  163  155   3      -1  258  253   4       0   47   25   8
 12  155  163   5        1  307  298   4       0  390  379   5       1  247  246   4
 13   90   93   6        2  260  264   4       1   63   79   6       2  377  380   5
                         3  347  344   4       2  368  359   5       3  349  336   5
 0  7  1                 4  434  434   4       3  327  330   4       4  212  199   4
                         5  487  489   5       4   82   54   6       5  290  299   4
-14   41   51   9        6   31    2   9       5  106  129   5       6  305  294   4
-13  137  142   5        7   13    3  16       6  -30    9  10       7  215  219   4
-12  179  179   4        8  427  425   5       7  175  166   5       8   11   55  20
-11  116  116   5        9  155  154   4       8  117  109   5       9  -44   26   8
-10   23   30  12       10   54   71   8                            10  221  210   5
 -9  908  911   8       11  -59    6   5      0  13  1
 -8  332  340   4       12    7   44  24                            1 -11  1
 -7   31   47   8                             -8   38   42  10
 -6  581  585   5       0  10  1              -7  190  174   5       0  287  283   4
 -5   97   95   4                             -6  271  270   4       1  122  134   4
 -4  406  412   4      -12  225  208   5      -5   67   78   7       2  129  147   4
 -3   84   86   4      -11  127  127   5      -4   45   16   8       3   49   83   7
 -2   98  119   3      -10   55   59   8      -3  345  350   5       4   27   30  11
 -1  171  171   3       -9   64   66   7      -2  340  335   5       5  499  493   5
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  2  492  509   5       -6  611  602   6       1  224  221   4       8  117  125   5
  3   59   58   4       -5  288  280   4       2  305  309   4       9  -49    6   6
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  8  205  215   4        0  499  498   5       7   24   18  14
  9  225  221   4        1   57   59   6                             0   19   13  10
 10   30   22  11        2  203  210   4      0  14  1               1  254  255   4
 11   94   91   5        3  457  457   5                             2  202  197   4
 12  225  225   5        4  213  214   4      -7  223  202   5       3  308  309   4
 13   68   51   7        5  369  361   4      -6  123  134   5       4  136  130   4
                         6  192  182   4      -5  178  184   5       5  -29   23   9
 0  8  1                                      -4  170  163   5       6  199  211   4
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  7  444  445   5        0   35   21   6        1  313  334   3       12   97   95   5
  8  118  119   5        1  238  250   3        2  251  281   2       13  216  213   4
  9  -35    9   9        2  679  686   6        3  689  695   6       14  120  118   5
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 11   19   10  16        4  771  758   7        5  209  214   3
 12   99  109   6        5  960  942   8        6  174  168   3           1    2    1
                         6   20    4  10        7  401  395   4
      1   -9   1         7  567  551   5        8  209  212   3      -15  272  266   5
                         8  487  483   5        9  538  539   5      -14   50   50   9
  0  298  295   4        9  186  185   4       10  474  470   5      -13   45   56   9
  1 1022 1015   9       10  -36    1   7       11   37   39   7      -12  267  256   4
  2   78   81   4       11  172  175   4       12  317  320   4      -11  131  119   4
  3  194  192   3       12   93  108   5       13   75   79   6      -10  217  213   4
  4  441  450   5       13  115  125   5       14  379  378   5       -9  180  175   4
  5  549  555   5       14  108  106   6       15  109  105   6       -8  -24    4   9
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  7  126  118   4                                  1    0    1       -6  772  765   7
  8  121  122   4           1   -4   1                               -5  802  790   7
  9  -32   48   9                            -15  186  174   5       -4 1506 1519  13
 10   38   27   9        0  397  403   4     -14  -26   31  13       -3  685  641   6
 11  -28   34  11        1  301  309   3     -13  271  274   4       -2  529  528   4
 12   47   71   9        2  770  782   6     -12  -39    2   8       -1  570  580   5
 13  117  122   5        3  187  191   3     -11   77   72   5        0  748  756   6
                         4  459  459   4     -10  139  139   4        1  -11   12  10
      1   -8   1         5  201  202   3      -9  205  207   4        2   11   23   9
                         6 1110 1106   9      -8   47   53   5        3  324  329   3
  0  297  304   4        7  369  358   4      -7  399  402   4        4  505  507   4
  1  698  683   6        8  158  151   3      -6  472  459   4        5  888  876   7
  2  414  420   4        9  183  177   4      -5  257  261   3        6  297  285   3
  3  341  354   4       10   57   70   6      -4  232  224   3        7  400  399   4
  4   38   43   7       11   57   72   6      -3   43   48   5        8  168  164   3
  5   70   73   5       12   72   73   6      -2 1104 1068   9        9  163  167   3
  6  228  233   4       13  287  296   5      -1  134  112   2       10  368  363   4
  7   39   38   7       14   14   42  18       1  219  207   2       11  338  332   4
  8  340  348   4       15  291  285   5       2  860  865   7       12   24   47  13
  9  333  327   4                             3  969  954   8       13  153  152   4
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 11  357  373   5                             5  590  587   5       15  269  258   5
 12  245  237   5        0  249  254   3      6  633  631   6
 13  167  159   5        1  168  171   2      7   63   72   4           1    3    1
                         2  244  250   3      8  719  727   6
      1   -7   1         3 1852 1859  15      9  570  559   5      -15  147  152   5
                         4  227  236   3     10  123  126   4      -14  250  255   5
  0  402  417   4        5  565  569   5     11   65   67   6      -13   22   36  13
  1  101   82   3        6  475  466   4     12   60   82   6      -12  398  389   5
  2  254  257   3        7  646  667   6     13  416  410   5      -11  299  290   4
  3  210  209   3        8  118  137   3     14  222  220   4      -10  131  123   4
  4  167  153   3        9  472  462   5     15  295  290   5       -9   52   28   6
  5  152  149   3       10  273  268   4                           -8  288  294   4
  6   51   30   6       11  252  247   4         1    1    1       -7  257  244   3
  7  289  284   4       12  110  124   5                           -6  642  623   6
  8  366  361   4       13  351  353   5     -15   99  108   6       -5  566  572   5
  9   87   79   5       14  -46   19   7     -14  254  241   5       -4 1414 1408  12
 10  136  147   4       15   87   98   6     -13  313  304   5       -3  315  322   3
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 13  -35   30  10                            -10  554  555   5        0  885  869   7
 14  125  132   5        0 1175 1149  10      -9  129  130   4        1  542  536   4
                         1  698  683   6      -8  138  137   3        2  369  365   3
      1   -6   1         2  243  238   2      -7  440  431   4        3  495  492   4
                         3  812  796   7      -6  228  240   3        4 1131 1148   9
  0  206  193   3        4  298  277   3      -5  770  765   7        5  124  121   3
  1   20    1   9        5  419  434   4      -4  346  336   3        6  633  609   6
  2  509  511   5        6  166  165   3      -3  734  725   6        7  173  193   3
  3  334  335   4        7  156  159   3      -2  212  202   2        8  557  573   5
  4  391  403   4        8  -39   24   5      -1   28   23   6        9  268  264   4
  5  394  404   4        9  497  501   5       0  252  256   2       10  572  566   6
  6  321  312   4       10  430  426   5       1   42    0   3       11  131  129   4
  7  -21   40  10       11  502  501   5       2  494  506   4       12   76   68   6
  8   79   60   4       12  -45   12   7       3  809  759   7       13  218  216   4
  9  157  153   4       13  148  161   5       4 1322 1325  11       14   74   86   7
 10   98  101   5       14  284  271   5       5  207  193   3       15  106   99   6
 11  189  197   4       15  250  245   5       6 1113 1118   9
 12  135  135   5                             7  759  768   7           1    4    1
 13  454  455   5           1   -1   1        8  284  281   4
 14  197  193   5                             9  413  413   4      -15  -32   34  11
                         0  412  436   3     10  142  139   4      -14   54   58   8
      1   -5   1                             11  204  190   4      -13  164  186   5
```

Tetrakis(pentafluorophenyl)-beta-octachloroporphyrin

```
-12    78    98    6        1   504   497    4      -13    60    73    8        1   12    1
-11   200   191    4        2   377   358    4      -12   -29     5   12
-10    78    88    5        3   895   875    8      -11   -57     3    5      -10    55    56    8
 -9   510   509    5        4   108   113    3      -10   111   103    5       -9   226   208    5
 -8   220   234    3        5   267   270    3       -9    40    69    9       -8   -17    48   16
 -7   341   341    4        6   433   432    4       -8   134   142    4       -7    55    41    7
 -6   887   873    8        7   104   112    4       -7    35    35    8       -6   220   203    4
 -5   170   156    3        8   -26    27    9       -6   314   313    4       -5    44    57    8
 -4   129   131    3        9   172   170    4       -5   210   212    4       -4   165   165    4
 -3   808   814    7       10    89    86    5       -4   666   665    6       -3   438   441    5
 -2   444   449    4       11   425   409    5       -3   476   487    5       -2    98    91    5
 -1  1087  1097    9       12   179   196    4       -2   549   547    5       -1    44    44    8
  0   200   213    2       13    63    50    7       -1   106   111    4        0   213   219    4
  1   304   292    3       14    43    53   10        0   228   218    3        1   242   234    4
  2   348   343    3                                  1   482   475    5        2   288   287    4
  3   447   435    4           1   7   1              2   406   403    4        3    93    86    5
  4   426   437    4                                  3   202   201    3        4   435   424    5
  5   544   536    5      -14    92    92    6        4   148   141    4        5   109   115    5
  6   236   246    3      -13    11    36   20        5    92    94    4        6   200   193    4
  7   262   258    3      -12    95   120    6        6   390   385    4        7   253   255    4
  8   436   438    4      -11   117   113    5        7   266   268    4        8    87    91    6
  9   386   388    4      -10   162   162    4        8   156   147    4        9   -18    31   16
 10   105   106    4       -9   115   101    4        9    40    35    9
 11   -19    48   13       -8    56    60    6       10     8    19   19        1   13    1
 12   362   358    5       -7   -30    17    8       11    29    63   12
 13   374   359    5       -6   661   648    6       12    39    51   11       -9   217   221    5
 14     8    38   23       -5   395   419    4                                 -8   187   178    5
 15   226   216    5       -4    33    52    7           1   10    1           -7   109   107    5
                          -3   281   269    3                                 -6   119   138    5
     1   5   1            -2    91    87    3      -12   197   187    5       -5    85    77    6
                          -1   964   983    8      -11    48    75    8       -4   175   168    4
-14    94    95    6        0   -22    24    8      -10   498   497    5       -3    15    38   16
-13   -33    12   10        1   422   403    4       -9   -34    10    9       -2   123   101    5
-12   -56     8    5        2    93    95    3       -8   -48    12    6       -1   145   149    4
-11    21     5   12        3   294   279    3       -7   108   115    5        0   491   496    5
-10   357   359    4        4   304   314    3       -6    70    71    5        1    41     8    9
 -9   299   300    4        5   176   179    3       -5   403   407    4        2   204   199    4
 -8   284   262    4        6   492   491    5       -4   153   152    4        3    32    41   10
 -7   486   469    5        7   461   468    5       -3   366   353    4        4    51    53    8
 -6   207   205    3        8    65    69    5       -2   127   132    4        5    81    83    6
 -5   130   101    4        9   338   348    4       -1   138   135    4        6    49    74    7
 -4    20    30    9       10   193   187    4        0   353   355    4        7   133   130    5
 -3   -19     9    8       11   129   127    5        1   390   382    4        8   174   181    5
 -2   569   575    5       12   256   259    5        2   449   457    5
 -1   225   218    3       13    31    15   12        3    50    56    6        1   14    1
  0   572   568    5                                  4   246   254    4
  1   189   178    2           1   8   1              5    90    89    5       -7    82    95    6
  2   867   879    7                                  6   248   271    4       -6   213   205    5
  3  1141  1140   10      -13   109   100    6        7    58    39    7       -5   232   228    5
  4   342   329    3      -12   153   141    5        8   190   176    4       -4   110   100    5
  5  1175  1157   10      -11   372   387    5        9   330   330    5       -3   251   246    4
  6    54    66    5      -10   271   276    4       10   245   246    5       -2    23     6   13
  7    42    49    5       -9    88    94    5       11    57    67    8       -1   154   151    4
  8   256   257    4       -8   126   132    4                                  0    68    38    6
  9   412   416    4       -7    82    97    5           1   11    1            1   258   257    4
 10   168   168    4       -6   380   386    4                                  2   370   352    5
 11   113   119    5       -5   577   582    5      -11   245   245    5        3    96    68    5
 12   121   135    5       -4   669   673    6      -10   107   109    5        4   167   158    5
 13   174   149    5       -3   269   259    3       -9    -5    34   24        5    45    54    9
 14   229   231    5       -2   419   433    4       -8   319   328    4        6    75    60    7
                          -1    42    59    4       -7   377   376    5
     1   6   1             0   753   768    7       -6   180   174    4        1   15    1
                           1    17    27    9       -5   191   204    4
-14   113   107    6        2   152   150    3       -4   112   125    4       -4   164   157    5
-13   151   147    5        3   225   230    3       -3   203   205    4       -3   103    90    5
-12   -63    10    5        4    64    35    5       -2   357   341    4       -2   178   185    5
-11   327   337    4        5   352   341    4       -1   275   269    4       -1   388   383    5
-10   159   153    4        6   101    87    4        0   516   509    5        0   138   154    5
 -9   176   162    4        7   211   203    4        1   137   134    4        1   114   103    5
 -8   212   208    4        8   134   132    4        2    27    48   10        2   117   113    5
 -7   251   244    3        9   130   115    4        3   132   125    4        3   236   224    5
 -6   609   596    6       10   220   224    4        4   205   207    4
 -5   412   414    4       11   -43     3    8        5    74    68    6        2  -14    1
 -4   189   195    3       12   188   180    5        6    55    66    7
 -3   208   205    3       13    85    84    6        7   200   194    4        0   141   138    5
 -2   320   320    3                                  8    84    80    6        1   162   153    5
 -1  1128  1128    9           1   9   1              9    86    73    6        2   119   112    5
  0   739   721    6                                 10   193   208    5
```

Tetrakis(pentafluorophenyl)-beta-octachloroporphyrin

```
3  268  260   5

   2 -13   1

0  176  160   5
1   90   82   6
2   39   42  10
3  265  253   5
4  136  118   5
5  108   93   5
6   41   23  10
7   84   66   6

   2 -12   1

0  128  120   5
1  205  190   4
2   -4   29  24
3   46   57   8
4  227  229   4
5   96  104   5
6   24   42  13
7  302  295   5
8  163  155   5
9  291  266   5

   2 -11   1

0   41   53   9
1  330  324   4
2   35   52   9
3  -37    5   7
4   85   94   5
5  299  286   4
6  129  123   5
7   76   77   6
8  148  144   5
9   44   57   9
10  32   46  12

   2 -10   1

0  392  389   4
1   73   69   5
2  -11   25  16
3  133  143   4
4  139  148   4
5   17   20  15
6   44   46   7
7  301  296   4
8  -30   20  10
9   94   98   5
10 153  151   5
11 297  290   5
12  77   74   7

   2  -9   1

0  -28    2   8
1  158  158   4
2  287  292   4
3  193  197   4
4   93  102   4
5  336  328   4
6  537  543   5
7  160  161   4
8  192  183   4
9  109  114   5
10 265  255   4
11 326  311   5
12 -13   12  18

   2  -8   1

0   44   36   6
1  498  513   5
2   88   99   4
3   56   38   5
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4  467  458   5
5  545  551   5
6  210  209   4
7   92   88   4
8   30   48   8
9  163  165   4
10 156  161   4
11 -21   17  14
12 169  177   5
13  53   58   8

   2  -7   1

0  275  274   3
1  572  583   5
2  390  385   4
3  485  475   5
4  267  257   3
5  139  135   3
6  549  555   5
7    6   27  19
8  155  157   4
9  417  405   5
10 128  121   4
11 -36    0   9
12 112  114   5
13 244  248   5
14 150  146   5

   2  -6   1

0   78   86   4
1  354  355   4
2  279  262   3
3   25   18   8
4  244  243   3
5  530  534   5
6  511  516   5
7  221  219   3
8  653  641   6
9  353  358   4
10 211  198   4
11 -34   21   9
12  -4   50  24
13  61   61   7
14  38   46  10

   2  -5   1

0  271  278   3
1  468  455   4
2  361  354   4
3  210  208   3
4  227  243   3
5   58   71   4
6  322  321   4
7  154  148   3
8  270  277   4
9  445  442   5
10 265  272   4
11 533  524   5
12  99  117   5
13 -15   26  17
14 -22   45  14
15 122  115   6

   2  -4   1

0  266  262   3
1  465  481   4
2  653  659   6
3  906  926   8
4 1199 1217  10
5  302  321   3
6  273  264   3
7  952  972   8
8  430  436   4
9  645  652   6
```

```
10 326  327   4
11  33   56   9
12 -11   38  19
13 217  225   4
14 -38   17   9
15 -35    4  11

   2  -3   1

0  936  944   8
1  497  500   4
2   72   63   3
3  628  622   5
4  952  916   8
5  553  567   5
6  911  873   8
7   25   23   8
8  109  119   4
9  276  279   4
10  28   13  10
11 245  244   4
12 262  262   4
13 258  263   4
14 110  108   5
15  55   64   7

   2  -2   1

0 2153 2167  18
1   91   84   3
2  365  353   3
3  900  892   7
4 1253 1245  10
5  863  851   7
6  246  237   3
7  314  318   3
8  -18   34  11
9   93   99   4
10 304  309   4
11 650  644   6
12  39   56   9
13  54   91   8
14 166  167   5
15 -30   38  12

   2  -1   1

0 1525 1490  13
1   61   45   3
2  341  330   3
3  300  273   3
4 1261 1271  10
5  986  983   8
6  371  360   4
7  605  582   5
8  133  146   3
9  244  255   4
10 178  184   4
11  99  109   4
12 276  282   4
13 168  185   4
14  72   74   6
15 260  238   5
16  66   62   8

   2   0   1

-14 208  182   5
-13 209  202   5
-12 -30   13  11
-11 -24   18  12
-10  27   40  11
-9   74   67   5
-8  256  249   4
-7  462  441   5
-6   51   53   5
-5 1037 1059   9
-4  455  469   4
```

```
-3  543  541   5
-2 1345 1337  11
-1 1372 1340  11
0 1956 1966  16
1  293  284   3
2  387  340   3
3   84   84   3
4  184  174   2
5  207  204   3
6  717  707   6
7  100   66   3
8  179  185   3
9  594  599   6
10 -41   15   6
11  20   32  12
12 -47    4   6
13 387  389   5
14 163  171   5
15 205  206   5
16  91   95   6

   2   1   1

-14 -20   26  13
-13 225  231   4
-12 122  102   5
-11  71   73   6
-10 119  120   4
-9  368  369   4
-8  -34   25   7
-7  257  242   3
-6   81   77   4
-5  555  582   5
-4  195  197   3
-3  710  700   6
-2  466  453   4
-1  438  432   4
0   22   11   7
1  144  154   2
2  288  270   3
3  183  160   2
4  163  160   2
5  604  619   5
6 1114 1128   9
7  175  187   3
8  597  607   5
9  637  625   6
10  18   34  12
11 197  202   4
12 325  338   4
13 -34   24   9
14 125  126   5
15 267  269   5
16  44   49  10

   2   2   1

-14 291  285   5
-13 138  125   5
-12 125  120   5
-11 205  216   4
-10 458  455   5
-9  205  214   4
-8  500  486   5
-7   82   81   4
-6  135  132   3
-5  258  262   3
-4  976  968   8
-3  640  631   5
-2 1174 1144  10
-1   62   51   3
0  454  399   4
1  135  144   2
2   27    5   7
3  585  584   5
4   57   50   4
5   91   87   3
6  340  331   3
```

Tetrakis(pentafluorophenyl)-beta-octachloroporphyrin

```
   7   168   169   3        -14   248   239   5        0    25    70   8       -11   235   231   5
   8   349   359   4        -13    34    54  11        1   206   193   3       -10    84    81   6
   9   328   311   4        -12   188   182   4        2   252   255   3        -9    69    70   6
  10   413   413   4        -11    79    85   6        3   365   384   3        -8   121   129   5
  11   274   264   4        -10    58    50   6        4   285   291   3        -7   150   149   4
  12   153   168   4         -9   312   314   4        5   561   557   5        -6   380   378   4
  13   381   369   5         -8   458   459   5        6   233   252   3        -5   448   462   5
  14    22    10  13         -7   605   615   6        7   638   640   6        -4   -38     1   6
  15   135   151   5         -6   569   584   5        8   195   197   4        -3   173   171   4
                            -5   620   594   6        9   323   317   4        -2   356   353   4
      2   3   1             -4   118   117   3       10   658   649   6        -1   154   154   3
                            -3   143   131   3       11    87    95   5         0    64    80   5
 -14   307   296   5        -2   848   852   7       12    73    71   6         1   185   179   3
 -13   117   124   5        -1   743   756   6       13   165   163   5         2    91    93   4
 -12   291   290   4         0   358   357   3       14   231   235   5         3   903   917   8
 -11   545   539   6         1   124   122   3                                  4    60    62   5
 -10   369   378   4         2  1150  1157  10          2   8   1                5   166   165   4
  -9   261   263   4         3  1840  1829  15                                  6   250   254   4
  -8   237   239   4         4   532   534   5       -13   100   105   6         7   303   280   4
  -7   368   377   4         5   810   789   7       -12   -42     7   8         8   181   169   4
  -6   150   176   3         6   258   259   3       -11   263   265   4         9    83    82   6
  -5   267   283   3         7    68    73   4       -10   131   131   5        10    59    63   7
  -4   298   278   3         8    86    94   4        -9   211   218   4        11    24    51  14
  -3  1246  1238  10         9    90    92   4        -8   319   324   4        12   257   249   5
  -2  1351  1362   9        10    66    74   6        -7   378   374   4
  -1   210   198   2        11    52    78   7        -6   247   238   4          2  11   1
   0   157   144   2        12   552   562   6        -5   337   344   4
   1   271   281   3        13   173   187   5        -4    46    33   6       -11   124   105   5
   2  1010   968   8        14   274   258   6        -3   413   414   4       -10    86    83   6
   3  1283  1277  11        15    72    88   7        -2   114   117   3        -9    77    81   6
   4  1052  1060   9                                 -1   631   645   6        -8   200   205   4
   5   144   150   3          2   6   1               0   315   319   3        -7   366   369   5
   6    -6    12  16                                  1   -35    14   5        -6   326   327   4
   7   355   358   4        -14     6    28  24        2    85   101   4        -5   233   233   4
   8   253   245   3        -13   160   174   5        3    41    52   6        -4    61    49   6
   9   865   864   8        -12    99   106   5        4   114   109   3        -3    75    90   5
  10   115   117   4        -11   227   220   4        5     7    22  16        -2    51    45   6
  11    70    76   6        -10   176   188   4        6   713   705   6        -1   105    95   4
  12   325   332   4         -9   612   606   6        7   354   364   4         0    84    99   5
  13   434   432   5         -8    35    37   8        8   170   175   4         1   255   258   4
  14   -17     6  16         -7    48    19   6        9   260   259   4         2   444   442   5
  15    38    29  11         -6    69    80   4       10   224   237   4         3   451   443   5
                            -5   300   301   3       11    77    74   6         4   447   444   5
      2   4   1             -4   387   389   4       12   261   264   5         5   382   383   5
                            -3   565   546   5       13   355   371   5         6   152   156   4
 -14    58    61   8        -2    64    32   4                                  7   231   236   4
 -13   116   102   5        -1  1090  1110   9          2   9   1                8   508   504   5
 -12   121   120   5         0   556   557   5                                  9   261   264   4
 -11    91   104   5         1    84    93   3       -12    34    47  11        10    82    74   6
 -10   102    90   5         2    67    62   4       -11   103   111   5        11    68    73   7
  -9   369   377   4         3   708   687   6       -10   -38    12   8
  -8   300   289   4         4  1794  1778  15        -9   -33     7   8          2  12   1
  -7   572   575   5         5   770   756   7        -8   415   417   5
  -6    73    87   4         6   347   345   4        -7   140   131   4       -10   229   217   5
  -5   532   516   5         7   189   211   3        -6   527   532   5        -9    98   105   6
  -4  1405  1399  12         8   393   392   4        -5    73    71   5        -8   -39    17   8
  -3   638   658   5         9   667   674   6        -4    63    73   5        -7   120   103   5
  -2   625   622   5        10   551   551   6        -3   244   250   3        -6   -44    12   7
  -1   326   332   3        11   -26     6  11        -2   542   525   5        -5   429   448   5
   0   482   484   5        12   105    95   5        -1   379   356   4        -4   263   274   4
   1   688   694   6        13    62    82   7         0   970   975   8        -3   120   130   4
   2  1085  1093   9        14   146   152   5         1   270   270   3        -2   216   224   4
   3  1598  1604  13                                  2   -43     3   5        -1   324   332   4
   4   164   162   3          2   7   1               3   -45    52   6         0    59    57   6
   5    63    79   4                                  4   797   818   7         1   215   223   4
   6   343   341   4        -13   151   146   5        5   143   165   4         2   154   167   4
   7   207   219   3        -12   410   394   5        6   358   360   4         3   167   168   4
   8    30    28   8        -11   102   103   5        7   387   387   4         4   302   300   4
   9   213   210   4        -10   118   110   5        8   201   193   4         5    71    80   6
  10   276   268   4         -9    63    48   6       10   160   152   4         6   -17    35  15
  11   122   140   4         -8   287   281   4       11   118   125   5         7   174   183   4
  12   264   260   4         -7   605   601   6       12    41    56  10         8    89    91   6
  13    90    96   6         -6   160   170   3       13    28    29  14         9    90    95   6
  14   210   198   5         -5   -34    21   5                                 10   123   125   5
  15    58    49   8         -4   231   248   3         2  10   1
                            -3   355   343   4                                    2  13   1
      2   5   1             -2   509   510   5       -12   -37    25  10
                            -1   163   175   3                                  -9   153   155   5
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 -8   -41     2   8      6   104   120   5      4   310   305   4      7   325   324   4
 -7   -19    25  15      7   -15     1  17      5   131   139   3      8   240   243   3
 -6   335   313   5      8   -31     2  10      6   203   222   3      9     8    17  17
 -5   368   363   5      9   149   151   5      7   132   126   4     10   195   194   4
 -4    13    23  17     10   209   198   5      8   347   333   4     11   560   557   6
 -3   329   324   4                             9   527   536   5     12   108   115   5
 -2   597   585   6      3  -10   1            10   177   159   4     13   -34    30   9
 -1    51    42   7                            11   252   242   4     14   225   215   5
  0   122   124   4      0   243   242   4     12    61    85   7     15   260   251   5
  1   595   597   6      1   372   368   5     13    55    66   8
  2    44    50   8      2   265   263   4     14   281   275   5      3  -1   1
  3   -37     5   8      3   171   186   4
  4    77    82   6      4   -38     6   8      3  -5   1             0   608   608   5
  5   186   184   4      5    30    15  11                           1  1164  1156  10
  6   -44    34   7      6   215   195   4      0  1296  1282  11     2   798   797   7
  7   161   165   5      7   103    96   5      1   256   234   3      3    37     3   5
  8    83   108   6      8   -34    32   9      2   470   478   4      4   717   720   6
                         9   179   182   4      3   180   189   3      5    13    26  11
  2  14   1             10    69    81   6      4   654   652   6      6   131   137   3
                        11    40     8  10      5   600   596   5      7   157   161   3
 -7    50    63   9                             6   442   446   4      8   467   469   3
 -6   141   129   5      3  -9   1             7   372   366   4      9   479   479   5
 -5   227   222   4                             8   151   145   4     10   215   208   4
 -4   223   225   4      0   336   347   4      9    43    33   7     11   -28     6   9
 -3    44    33   9      1   245   239   4     10   304   309   4     12    88    99   5
 -2    99    76   5      2   175   178   4     11   298   292   4     13    84    95   6
 -1    25    38  13      3   168   171   4     12   100   103   5     14    33    46  11
  0   221   211   4      4   111   105   4     13     8    46  21     15   330   324   5
  1    48    48   8      5   144   138   4     14   103    95   6     16   252   234   5
  2   217   209   4      6   521   504   5     15   147   138   5
  3   372   373   5      7    34    13   9                            3   0   1
  4   211   220   4      8    54    55   7      3  -4   1
  5    64    74   7      9   407   413   5                          -14    47    22  10
  6   306   286   5     10    69    66   6      0    95   103   3    -13   -38    15   9
  7    48    27   9     11   183   194   5      1   291   302   3    -12   281   285   5
                        12   167   164   5      2   155   160   3    -11   251   252   4
  2  15   1                                     3   520   521   5    -10   166   159   4
                         3  -8   1             4   506   522   5     -9   192   197   4
 -5    20    25  14                             5   283   292   3     -8    88    91   4
 -4   252   255   5      0   101   103   4      6   115   124   3     -7   116   125   4
 -3    71    67   7      1   178   177   4      7   556   569   5     -6   348   345   4
 -2    59    59   7      2    94   114   4      8   362   369   4     -5   360   356   4
 -1    33    10  11      3   218   216   4      9    91    91   4     -4    46    38   5
  0    63    47   7      4    57    63   6     10   -21     0  11     -3   830   821   7
  1   249   241   5      5   583   590   6     11   321   324   4     -2    54    45   4
  2    83    88   6      6    56    40   6     12    60    89   7     -1    46     8   4
  3    62    30   7      7   468   470   5     13   206   211   4      0   152   145   2
  4   174   178   5      8    81    89   5     14    98    99   6      1  2457  2436  20
                         9   409   389   5     15   357   345   5      2   384   374   3
  3  -13   1            10   218   216   4                            3   796   810   7
                        11   141   143   5      3  -3   1            4   301   303   3
  0   124   113   5     12   -29    27  11                            5   818   810   7
  1   241   241   5     13   231   211   5      0   605   591   5      6   445   445   4
  2   170   165   5                             1   853   864   7      7   169   183   3
  3   204   201   5      3  -7   1             2    20     6   8      8   762   774   7
  4   166   156   5                             3   161   159   3      9   230   238   4
  5   334   314   5      0    50    51   6      4   228   223   3     10   138   124   4
                         1    40     0   7      5   750   768   6     11   106   103   4
  3  -12   1            2     9     9  16      6   448   455   4     12    65    93   6
                         3   -12     2  13      7   107   106   3     13   164   158   4
  0    49    48   8      4    50    45   6      8    27    34   9     14    62    59   7
  1   215   208   4      5    42    44   7      9    30    11   7     15   -40    16   9
  2   208   211   4      6   359   359   4     10   461   459   5     16    85    79   6
  3   129   129   5      7   319   315   4     11   755   762   7
  4    82    83   6      8   287   291   4     12   100    96   5      3   1   1
  5   211   201   4      9   110   110   5     13    86    96   6
  6    29    15  12     10   409   402   5     14   167   154   5    -14   263   260   5
  7    54    46   8     11   172   175   4     15   -40    27   8    -13   224   211   5
  8    21     1  15     12   259   276   4                          -12   275   260   5
                        13   108   122   5      3  -2   1           -11   212   208   4
  3  -11   1            14   190   185   5                          -10     8    27  20
                                               0   576   560   5     -9   -12     8  16
  0   185   173   4      3  -6   1             1   409   411   4     -8    27    29  10
  1   129   133   5                             2   300   297   3     -7   115   106   4
  2   129   139   5      0   138   134   3      3   188   192   3     -6   212   211   3
  3   -29    18  10      1   124   129   3      4   747   758   6     -5   358   365   4
  4   308   314   4      2    29    38   6      5   357   372   4     -4    67    53   4
  5   147   148   4      3   103   100   3      6   125   144   3     -3   323   321   3
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 -2  227  230   3      8  286  274   4    -11  349  338   5      6  214  216   3
 -1 1947 1987  16      9  311  316   4    -10   80   90   6      7   56   52   6
  0 1856 1836  15     10  244  237   4     -9  189  184   4      8    9   28  17
  1  503  484   3     11   26   50  11     -8  416  417   5      9  243  252   4
  2  666  653   6     12  256  258   4     -7  370  367   4     10   35   51  10
  3  134  125   3     13  341  330   5     -6   95   90   4     11   23   37  12
  4  255  259   3     14   27    6  13     -5  263  261   3     12   65   81   7
  5  718  696   6     15  186  182   5     -4  127  114   3     13  236  227   5
  6   39   16   6                          -3  150  146   3
  7  941  954   8      3   4   1           -2  639  651   6      3   9   1
  8   72   57   4                          -1   63   53   4
  9  355  337   4    -14  -22   41  15      0  127  114   3    -12  178  181   5
 10  247  240   4    -13  -20   18  15      1   11   13  12    -11  156  175   5
 11  234  228   4    -12   23   36  12      2  257  265   3    -10  147  153   5
 12  279  279   4    -11   62   45   6      3  541  519   5     -9  134  137   4
 13  402  399   5    -10  392  390   5      4  446  430   4     -8   11    1  18
 14  201  194   4     -9  555  548   6      5  179  179   3     -7  684  689   6
 15   57   71   8     -8  241  248   4      6  590  578   5     -6  216  211   4
 16   62   59   8     -7  533  543   5      7  679  682   5     -5  308  312   4
                      -6  363  380   4      8  153  162   4     -4  320  319   4
  3   2   1           -5  907  918   8      9  476  465   5     -3  285  295   4
                      -4  116  119   3     10  331  322   4     -2  238  227   3
-14  101   81   6     -3  200  209   3     11   78   97   6     -1  238  234   3
-13   60   66   6     -2  577  587   5     12   88   89   6      0  461  463   5
-12  191  183   4     -1   22   23   8     13  208  209   5      1  410  416   4
-11  124  119   5      0   97   98   3     14  186  175   5      2  237  238   3
-10  231  234   4      1  360  367   3                          3  678  669   6
 -9  534  533   5      2 1819 1805  15      3   7   1           4   68   81   5
 -8  201  211   4      3  611  613   5                          5  187  202   3
 -7  312  303   4      4  554  549   5    -13   70   97   7      6  244  243   4
 -6  547  539   5      5   70   65   4    -12   43    0  10      7  258  255   4
 -5  249  246   3      6   64   74   4    -11  475  468   5      8  108  120   4
 -4  184  187   3      7    2   44  19    -10  166  142   4      9  178  173   4
 -3   15   39  12      8  462  460   5     -9   79   83   5     10   44   61   8
 -2  712  713   6      9  460  463   5     -8  160  166   4     11   45   70   9
 -1  224  224   3     10   31   28   9     -7  235  249   4     12  125  122   5
  0   95   86   3     11  -12   55  17     -6  219  204   3     13  269  267   5
  1  681  653   6     12  132  137   5     -5  113  116   4
  2 1035 1004   9     13  304  303   5     -4  526  520   5      3  10   1
  3  611  611   5     14  276  286   5     -3  556  572   5
  4  642  638   5     15  252  252   5     -2   27   29   8    -11   72   68   7
  5 1252 1249  10                          -1  836  843   7    -10   39   51  10
  6  250  273   3      3   5   1            0  366  343   4     -9  -15   43  17
  7  125  124   3                          1  641  607   6     -8   19   35  14
  8  342  339   4    -13   35   54  10      2   60   50   4     -7  155  164   4
  9  222  217   4    -12  247  256   5      3  570  599   5     -6  220  231   4
 10  456  454   5    -11  132  137   5      4  188  183   3     -5  108  100   4
 11  443  422   5    -10  166  181   4      5    4   23  18     -4  108  107   4
 12  486  490   5     -9  212  208   4      6  289  294   4     -3  446  438   5
 13   25   41  13     -8  561  555   5      7   93   92   4     -2  569  563   5
 14    1   31  27     -7  117   88   4      8  296  294   4     -1  208  198   3
 15   61   79   8     -6  739  735   7      9  240  235   4      0  -31    9   7
 16   35   30  10     -5  154  158   3     10  262  275   4      1  239  231   4
                      -4   95  108   3     11  167  173   4      2  301  309   4
  3   3   1           -3   23   21   8     12  129  124   5      3  132  126   4
                      -2  675  679   6     13  109  122   5      4  401  404   4
-14   85   78   6     -1  905  884   8     14   41   51  10      5  160  155   4
-13   36   59  10      0  716  711   6                          6  209  204   4
-12   77   78   6      1  693  693   6      3   8   1            7   48   31   7
-11  100   87   5      2  624  609   5                          8  366  356   5
-10  383  384   5      3  298  303   3    -12   15   38  18      9  103  124   5
 -9  404  420   5      4  288  283   3    -11  105  108   5     10  233  246   4
 -8  211  211   4      5  305  291   3    -10   11   39  19     11   58   52   8
 -7  252  260   4      6  518  531   5     -9  187  188   4     12   55   54   8
 -6  792  793   7      7  225  248   3     -8  378  392   4
 -5   64   52   3      8  418  425   4     -7  -11   21  16      3  11   1
 -4  448  445   4      9   59   56   5     -6  577  578   5
 -3   32    2   6     10   37   45   8     -5   88   93   4    -11  221  213   5
 -2  102   96   3     11  127  139   4     -4  442  445   4    -10  193  186   5
 -1  846  835   7     12  197  203   4     -3  331  330   4     -9   28   47  12
  0   98   89   3     13  103  102   5     -2  242  240   3     -8  195  197   4
  1  723  705   6     14  -23    8  14     -1  191  183   3     -7  212  211   4
  2  209  210   2     15   98  111   6      0  473  490   4     -6   96  101   5
  3 1858 1832  16                          1   78   92   4     -5   70   72   6
  4  150  149   3      3   6   1            2   26    5   8     -4   16   47  14
  5  254  264   3                          3   43   64   5     -3  252  263   4
  6  524  501   5    -13  -19   34  16      4  172  170   3     -2  383  371   4
  7  577  564   5    -12  266  272   5      5  423  426   4     -1  192  198   4
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  0   143   130    4        -5    31    36  12         5   130   127    4        14   193   192    5
  1   102   103    4        -4   -18    20  16         6   -15    14  13        15   165   176    5
  2   269   267    4        -3   -55     9   6         7   223   219    4
  3   191   183    4        -2   107   110   5         8   643   636    6         4   -3   1
  4   204   197    4        -1   381   391   5         9    93   100    5
  5   409   408    5         0    70    70   7        10   238   231    4         0   101    99    3
  6   235   245    4         1   172   160   5        11   142   135    5         1   149   149    3
  7   211   200    4         2   187   170   5        12    93    90    6         2    63    54    4
  8   -26    27   11         3   353   349   5                                   3   166   170    3
  9   305   288    5         4   117   121   5         4   -7   1                 4   377   371    4
 10   208   208    5         5   -29    27  12                                   5    74    59    4
 11    79    87    6                                   0   455   450    5         6   305   288    4
                            3   16   1                 1   310   312    4         7   213   210    3
  3   12   1                                           2    71    68    5         8   185   189    3
                            -1    53    54   8         3    56    73    5         9   581   588    6
-10    45     5   10         0   -30     0  11         4   -31     3    8        10     7    47   20
 -9   149   136    5         1    93    87   6         5    41    44    7        11    89    72    5
 -8    64    46    7                                   6    73    70    5        12   158   170    4
 -7    69    80    6         4  -12   1                7   337   330    4        13   105   111    5
 -6   146   152    4                                   8   163   148    4        14   172   182    5
 -5    14    19   16         0    49    70   8         9   224   233    4        15   279   266    5
 -4    31    41    9         1    83    86   6        10   179   167    4
 -3   -38    30    8         2    57    46   8        11    30    42   12         4   -2   1
 -2   535   541    5         3   101   107   5        12   153   155    5
 -1   310   321    4         4   290   293   5        13   305   300    5         0   416   408    4
  0   145   158    4         5    46    38   9                                   1   410   419    4
  1    59    61    6         6   132   128   5         4   -6   1                 2    12     9   11
  2   -25    19   10                                                             3   283   284    3
  3   143   148    4         4  -11   1                0   175   175    3         4   379   383    3
  4    41    73    8                                   1   -26     1    8         5   298   308    3
  5   181   179    4         0    44    26   9         2    52    34    5         6   243   239    3
  6   -10    46   19         1   241   254   4         3   321   313    4         7   125   126    3
  7    93   122    5         2   174   169   4         4   560   547    5         8   183   185    3
  8   350   340    5         3   162   160   4         5   278   273    4         9    42    44    7
  9   201   212    5         4   251   257   4         6   222   219    4        10   386   385    4
 10   238   235    5         5   169   171   5         7   176   177    4        11   375   373    5
                            6    98    91    5         8    54    51    6        12   -34     6    9
  3   13   1                7   107   112    5         9    79    82    5        13    38    55    9
                            8   -22    23   14        10   177   181    4        14    65    70    7
 -9   115   105    5         9    70    78    7        11   379   404    5        15   202   201    5
 -8    72    81    7                                  12   -32    29    8
 -7   193   184    5         4  -10   1               13   125   119    5         4   -1   1
 -6   266   255    4                                  14   386   374    5
 -5   143   140    5         0   100    96   5                                   0   369   344    4
 -4   -36     2    9         1   237   238   4         4   -5   1                 1   426   430    4
 -3   305   300    4         2    47    55   7                                   2   652   644    6
 -2   -22    14   13         3   -27    22  10         0    42    19    6         3   190   185    3
 -1   564   556    6         4   116   119   5         1   227   224    5         4   593   598    5
  0   143   152    4         5   131   128   5         2   718   707    6         5   412   418    4
  1   201   208    4         6   126   131   5         3   729   738    6         6   -11    54   13
  2    68    72    6         7   261   262   4         4   226   214    5         7   538   522    5
  3   249   259    4         8    81    91   6         5   -14    32   13         8   419   424    4
  4    19    28   14         9    36    38  11         6   144   148    3         9   380   372    4
  5   106   116    5        10    93   102   6         7   210   221    4        10   211   216    4
  6   190   200    4                                   8   330   331    4        11   290   284    4
  7   170   169    5         4   -9   1                9   271   272    4        12   386   397    5
  8   151   148    5                                  10    43    45    8        13   425   423    5
  9    39    39   10         0    32    33  10        11   -18    34   15        14   135   142    5
                            1    60    62    5        12   160   174    4        15   279   270    5
  3   14   1                2   440   430    5        13   -37    28    9
                            3    54    58    7        14   -33     5   11         4    0   1
 -7    44    57    9         4    18    10   12
 -6   242   238    5         5    57    38    7        4   -4   1               -13   234   234    5
 -5   103   111    5         6   766   777    7                                -12   198   206    5
 -4   -34     4    9         7    93    71    5        0   118   123    3       -11   -15    14   16
 -3    79    82    6         8   176   182    4        1    26    16    8       -10    -6    23   23
 -2   167   155    4         9   268   275    4        2    79    81    4        -9    42    31    8
 -1   313   310    4        10    41    36    9        3   161   152    3        -8   135   140    4
  0    36    49   10        11    14    21   18        4   485   509    5        -7   213   209    4
  1   249   244    4                                   5   527   516    5        -6   511   524    5
  2   362   362    5         4   -8   1                6   165   166    3        -5    53    20    5
  3    62    54    7                                   7   425   414    4        -4    26     3    8
  4    94   102    5         0   117   122    4        8   462   461    5        -3    38    29    6
  5   131   131    5         1   240   237    4        9   407   395    4        -2   733   725    6
  6   111   105    5         2    70    75    5       10   523   521    5        -1   572   573    5
  7    89    86    6         3   141   137    4       11   103   104    5         0  1019  1018    9
                            4   143   153    4       12   -57     0    5         1   648   665    6
  3   15   1                                         13   182   190    5         2    82    93    3
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3	225	221	3	15	37	24	11	-4	271	264	3	11	423	426	5
4	127	134	3	16	115	121	6	-3	161	174	3	12	103	71	5
5	52	60	5					-2	147	137	3	13	248	234	5
6	605	606	5	**4**	**3**	**1**		-1	514	529	5	14	-7	30	23
7	73	83	4					0	236	231	3				
8	105	113	4	-13	65	80	7	1	238	258	3	**4**	**8**	**1**	
9	134	126	4	-12	80	103	6	2	681	682	6				
10	564	551	5	-11	549	555	6	3	388	402	4	-12	29	37	13
11	175	170	4	-10	121	119	5	4	43	13	5	-11	136	133	5
12	113	120	5	-9	140	147	4	5	568	532	5	-10	460	455	5
13	213	230	4	-8	100	112	4	6	221	222	3	-9	85	71	6
14	128	122	6	-7	71	73	5	7	-10	17	15	-8	49	24	8
15	-41	6	7	-6	260	254	4	8	475	484	5	-7	572	577	6
16	-25	31	13	-5	437	445	4	9	250	255	4	-6	258	256	4
				-4	233	225	3	10	408	409	5	-5	294	302	4
4	**1**	**1**		-3	153	157	3	11	301	308	4	-4	555	555	5
				-2	214	221	3	12	442	441	5	-3	16	17	12
-13	-39	29	9	-1	139	125	3	13	280	288	5	-2	24	39	9
-12	-19	17	15	0	77	87	3	14	165	173	5	-1	37	30	6
-11	166	170	5	1	11	27	13	15	-33	13	11	0	398	412	4
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-9	171	164	4	3	511	499	5	**4**	**6**	**1**		2	175	173	3
-8	-25	25	10	4	538	561	5					3	93	112	4
-7	127	107	4	5	136	144	3	-13	116	121	6	4	191	193	3
-6	446	457	5	6	100	101	3	-12	-19	8	16	5	453	438	5
-5	130	119	3	7	162	168	3	-11	166	184	5	6	150	126	3
-4	278	263	3	8	221	220	3	-10	222	229	4	7	366	372	4
-3	101	107	3	9	306	310	4	-9	107	93	5	8	298	292	4
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-1	717	712	6	11	157	165	4	-7	371	375	4	10	99	100	5
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1	607	616	5	13	80	76	6	-5	192	200	3	12	-44	49	8
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3	261	264	3	15	15	59	18	-3	326	300	4	14	115	124	6
4	44	34	4					-2	425	428	4				
5	576	582	5	**4**	**4**	**1**		-1	316	334	3	**4**	**9**	**1**	
6	285	310	3					0	576	574	5				
7	76	86	4	-13	73	72	7	1	326	325	3	-11	156	171	5
8	136	134	3	-12	65	87	7	2	413	387	4	-10	164	162	5
9	580	570	5	-11	304	305	5	3	766	727	7	-9	13	35	17
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12	295	303	4	-8	15	27	15	6	419	408	4	-6	170	172	4
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16	-38	11	10	-4	666	677	6	10	454	457	5	-2	574	573	5
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-10	34	15	10	3	451	428	4	**4**	**7**	**1**		5	246	257	4
-9	-11	25	18	4	1423	1427	12					6	194	191	4
-8	125	117	4	5	331	320	4	-12	39	34	11	7	887	885	8
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0	435	425	4	13	74	87	6	-4	325	328	4	**4**	**10**	**1**	
1	834	835	8	14	-20	44	15	-3	102	110	3				
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3	85	71	3					-1	86	89	4	-10	29	54	12
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6	528	520	5	-13	-34	50	8	2	423	412	4	-7	-8	38	20
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8	93	87	4	-11	151	148	4	4	747	746	7	-5	190	189	4
9	487	479	5	-10	276	266	4	5	579	562	5	-4	-23	26	10
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13	171	175	4	-6	189	178	3	9	-17	34	13	0	318	304	4
14	57	46	8	-5	273	268	4	10	-41	11	7	1	437	440	5

Tetrakis(pentafluorophenyl)-beta-octachloroporphyrin

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  2  473  474  5      8   35   45 11      9   28   60 12      6  317  319  4
  3  110  107  4      9   52   66  8     10  162  159  5      7  282  284  4
  4   63   57  5                                              8  382  395  4
  5  255  248  4        4  14  1           5  -8  1           9  467  455  5
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  8  -37   36  8     -6  122  131  5      1  114  101  4     12  -33   38  9
  9  293  284  4     -5   45   57  9      2  354  362  4     13  100  111  6
 10   70   86  6     -4  227  235  4      3   89   86  5     14  185  191  5
 11   44   60  9     -3   53   43  6      4  334  327  4
 12  248  237  5     -2  203  198  4      5  156  172  4        5  -3  1
                    -1   54   74  7      6  339  340  4
    4  11  1          0  -42   10  7      7  144  146  4      0  557  554  5
                     1  112  124  5      8    6    3 21      1  344  350  4
-10  290  279  5      2  282  268  4      9  -35   17  9      2  193  174  3
 -9   80   83  6      3  163  143  4     10  357  345  5      3  231  231  3
 -8  187  198  4      4  -40   33  8     11   87   95  6      4   21   16  9
 -7  113  115  5      5    9   43 20     12  128  132  5      5  140  142  3
 -6  104   97  5      6  248  239  5                          6  121  117  4
 -5  469  486  5      7  111  102  5        5  -7  1          7  456  454  5
 -4   10    7 18      8   56   56  8                          8  390  403  4
 -3  183  197  4                          0   97   98  4      9  491  493  5
 -2  115  118  4        4  15  1           1  219  216  4     10  229  235  4
 -1   70   69  5                          2  222  233  4     11   51   47  7
  0  197  190  4     -5   24   29 14      3  -17   27 12     12   98   91  5
  1  107  111  4     -4  135  131  5      4  200  204  4     13  248  252  5
  2  690  698  6     -3   33   26 11      5   91   86  5     14   99  112  6
  3  296  296  4     -2  -40   13  8      6  172  174  4     15   19   19 17
  4   43   44  7     -1  130  139  5      7   86   75  5
  5  106  114  4      0   63   74  7      8   69   65  6        5  -2  1
  6  177  185  4      1   45   44  8      9  -30    3  8
  7  100  105  5      2  188  176  5     10   30   25 11      0  316  308  4
  8  415  411  5      3  121  113  5     11  314  315  5      1  308  321  3
  9  327  346  5      4  300  288  5     12  106  111  6      2  168  163  3
 10   99   95  5      5    8   15 22                          3  352  343  4
 11  117  114  5      6  216  211  5        5  -6  1          4  242  237  3
                                                             5   83   87  4
    4  12  1            4  16  1           0  226  223  4      6  101   85  4
                                          1  133  120  4      7  263  258  4
 -9  249  254  5     -1   92   93  6      2  325  324  4      8  335  333  4
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 -6  243  252  4                          5  166  170  4     11  188  188  4
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 -3  179  186  4      0  104  107  5      8   60   59  6     14  207  207  5
 -2  154  160  4      1   92   79  6      9  132  139  4     15  110  124  6
 -1  256  267  4      2  107  115  5     10   75   81  6
  0  162  166  4      3  104   99  5     11  138  129  5        5  -1  1
  1  263  289  4      4   67   81  7     12   11   27 20
  2   54   57  6      5   87   84  6     13  179  180  5      0  167  166  3
  3  303  299  4      6   35   29 10                          1  692  724  6
  4  131  123  4      7   94   99  6        5  -5  1          2 1019 1035  9
  5   74   89  6                                              3   68   81  4
  6   97  106  5        5 -10  1           0  198  193  3      4  373  369  4
  7  226  242  4                          1  272  257  4      5  538  540  5
  8  117  126  5      0   81   92  6      2   35   24  7      6   27   14  8
  9  205  187  5      1   72   65  6      3  324  320  4      7  473  464  5
 10   71   74  7      2   34   26 11      4  285  282  4      8  -23   27 10
                     3   42   45  9      5  329  331  4      9   35   50  8
    4  13  1          4   50   51  8      6  118  116  4     10   72   88  5
                     5   33   12  9      7  -12   27 14     11  110  123  5
 -8  285  274  5      6  -15    3 17      8  506  494  5     12   34   24 10
 -7  286  276  5      7  -26   30 12      9  183  185  4     13  239  243  4
 -6   70   37  6      8   48   62  9     10  199  188  4     14   46   58  9
 -5   64   63  6      9  187  177  5     11  142  142  5     15   67   78  7
 -4  259  251  4                         12  159  173  5
 -3  206  205  4        5  -9  1          13  -30    2 11      5   0  1
 -2  100  105  5                         14  -53   11  7
 -1  111  101  5      0  139  156  4                        -12   17   48 18
  0  115  119  5      1  123  124  5        5  -4  1        -11   44   39  9
  1  301  303  4      2   36   41 10                       -10   52   50  8
  2  -41    9  6      3   -3   14 24      0  528  516  5     -9   48   50  8
  3  259  268  4      4   -3   15 25      1  233  239  3     -8   21   45 14
  4  445  434  5      5  126  119  5      2   67   66  4     -7   96   83  5
  5   31   69 11      6  138  125  5      3   40   51  5     -6  205  201  4
  6   45   37  8      7  340  339  5      4  110  105  4     -5  533  530  5
  7  160  160  5      8   63   65  7      5  278  281  4     -4   42   16  6
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Tetrakis(pentafluorophenyl)-beta-octachloroporphyrin

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 -3  423  419   4        13  522  511   6        -2   40   32   5        14   90   90   6
 -2  790  795   7        14  312  301   5        -1  288  262   3
 -1   83   78   4        15   88   83   6         0  697  711   6         5   8   1
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  1  237  222   3         5   3   1               2   31   17   6       -11  150  140   5
  2  284  281   3                                 3  851  873   7       -10  286  277   5
  3  102  123   3       -12   65   53   7         4  703  717   6        -9  107   95   5
  4 1166 1150  10       -11  123  125   5         5  130  136   3        -8   45   33   8
  5  184  169   3       -10  378  380   5         6  220  221   3        -7  637  640   6
  6  219  212   3        -9   43   61   9         7  220  214   3        -6  243  218   4
  7   32   29   8        -8  206  221   4         8  123  115   4        -5  256  253   4
  8  363  354   4        -7  192  185   4         9  164  155   4        -4  -28    0   8
  9   66   66   5        -6  114  118   4        10  213  217   4        -3   45   43   6
 10  218  219   4        -5   87   93   4        11  248  250   4        -2  551  564   5
 11   64   55   6        -4   62   45   5        12  334  346   5        -1   96  100   4
 12  438  435   5        -3   91   88   4        13  238  234   4         0  111  127   3
 13  124  132   5        -2  589  583   5        14  200  194   5         1  296  302   4
 14  276  273   5        -1   38   44   6        15  -59   14   6         2  -19   24   9
 15  194  181   5         0  129  125   3                                 3   37   60   7
                         1   24   31   8         5   6   1                4   50   37   5
  5   1   1              2  124  129   3                                 5  331  331   4
                         3  341  333   4       -12  130  149   5         6  270  269   4
-12  121  132   5         4  263  262   3       -11   93   81   6         7  349  354   4
-11  -35   24  10         5  142  148   3       -10  -31   15  11         8  435  431   5
-10   66   81   7         6  430  410   4        -9   12   22  18         9  636  639   6
 -9  274  273   4         7  -23   24   9        -8  167  169   4        10   17   50  15
 -8  137  144   4         8   90   86   4        -7  520  511   5        11  339  348   5
 -7  128  128   4         9  162  160   4        -6   67   57   5        12  -35   41  10
 -6  443  448   5        10  594  590   6        -5  205  199   4        13   32   31  10
 -5  265  262   4        11  -46   14   6        -4   18    9  10        14   63   75   8
 -4   26   53   9        12  393  387   5        -3  376  373   4
 -3  105  104   4        13  291  290   4        -2   77   64   4         5   9   1
 -2  346  351   4        14  215  204   5        -1   73   59   4
 -1  193  185   3        15  153  145   5         0  494  486   5       -11   57   60   8
  0  472  469   4                                 1   56   65   4       -10   38   35  10
  1  382  391   4         5   4   1               2  394  396   4        -9  120  121   5
  2  691  697   6                                 3  279  292   3        -8  274  279   4
  3   84   78   3       -12   51   68   9         4   17   13  10        -7  245  229   4
  4  614  597   5       -11  238  232   5         5  833  838   7        -6  115  107   4
  5   25    0   9       -10   48   68   8         6   90   89   4        -5   35   32   9
  6  135  121   3        -9  153  145   4         7   14   27  13        -4   48   50   7
  7 1108 1109   9        -8    0   17  26         8  421  426   5        -3  258  267   4
  8  367  376   4        -7   55   48   6         9  177  181   4        -2  456  462   5
  9  771  794   7        -6  148  148   4        10  491  490   5        -1  331  332   4
 10  101  108   4        -5   14   13  14        11  103  112   5         0   60   55   5
 11  119  143   4        -4  165  164   3        12   86   90   6         1  318  322   4
 12   38   34   8        -3  417  421   4        13  165  148   5         2  150  150   3
 13  131  127   5        -2  193  195   3        14  301  292   5         3   98   85   4
 14   61   41   7        -1 1401 1386  12        15  227  209   5         4  567  565   5
 15  313  297   5         0   97   98   3                                 5  365  373   4
                         1  149  147   3         5   7   1                6   33   30   9
  5   2   1              2  318  313   3                                 7  108  103   4
                         3  242  241   3       -12   94   74   6         8   98  103   5
-12  176  158   5         4  586  596   5       -11  347  327   5         9   66   77   6
-11  -22   25  14         5  374  374   4       -10   97  109   6        10  -45   14   7
-10   88   70   6         6   66   57   4        -9   75   67   6        11   18   54  16
 -9  143  143   4         7  104  102   4        -8   52   45   7        12  145  152   5
 -8  258  256   4         8  298  299   4        -7  260  252   4        13  118  129   5
 -7  202  206   4         9  265  266   4        -6  572  590   6
 -6  139  131   4        10  -19    6  13        -5  286  274   4         5  10   1
 -5  142  143   4        11   38   63   8        -4  -24    9   8
 -4  134  127   3        12  146  147   4        -3   61   39   5       -10  112  105   5
 -3  365  337   4        13  127  140   5        -2  867  878   8        -9   23   68  14
 -2 1050 1050   9        14  286  289   5        -1  778  774   7        -8  117  125   5
 -1  468  447   4        15  172  165   5         0  211  216   3        -7   31   14  11
  0  498  495   5                                 1  502  484   5        -6  256  252   4
  1  173  172   3         5   5   1               2  299  289   3        -5  296  283   4
  2  195  187   3                                 3  262  261   3        -4  200  200   4
  3   48   39   5       -12   35   28  12         4  937  947   8        -3   61   70   6
  4  648  652   6       -11  172  162   5         5  234  228   3        -2  175  190   4
  5  120  135   3       -10  156  166   5         6  287  300   4        -1  305  316   4
  6  341  323   4        -9   10   23  20         7  469  462   5         0  185  185   4
  7  163  159   3        -8  347  340   4         8  395  391   4         1  294  300   4
  8   38   14   7        -7  188  191   4         9  -38   25   7         2  234  240   4
  9  284  278   4        -6  339  338   4        10  -33   25   9         3  465  462   5
 10  200  212   4        -5  468  475   5        11  402  400   5         4  182  184   4
 11  259  263   4        -4  133  121   3        12  -27   20  10         5  305  301   4
 12  150  147   4        -3   44   33   4        13   85   86   6         6  175  178   4
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 7   46   51   7      -4  372  369   5       6  251  248   4       0  394  394   4
 8   38   55   7      -3  252  239   4       7   42   41   9       1  143  134   3
 9  237  225   4      -2  254  242   4       8  143  146   5       2   15    4  12
10  400  408   5      -1  225  227   4       9   92  110   6       3  388  392   4
11   89   99   6       0   49   51   6      10  108   97   5       4   77   72   4
12  -47   16   8       1   83   92   6      11  236  229   5       5  533  527   5
                       2  193  174   4                             6   97   93   4
    5   11   1         3   68   82   6          6   -6   1         7  153  169   4
                       4   -3   32  25                             8  -15   20  14
-9  -30   25  11       5   80   74   6       0  287  291   4       9  185  184   4
-8  204  203   4       6   85   95   6       1  214  205   4      10   83   89   5
-7  215  218   4       7  206  199   5       2  119  130   4      11  251  254   4
-6  257  259   4       8  103   96   6       3   74   68   5      12  485  484   5
-5  156  140   4                             4  226  238   4      13   68   67   7
-4  426  427   5          5   15   1         5   82   89   5      14   70   65   7
-3   85   84   5                             6  258  257   4
-2  220  214   4      -4   76   80   7       7   69   64   6          6   -1   1
-1  189  199   4      -3  265  262   5       8  287  284   4
 0   80   87   5      -2  142  134   5       9  167  154   4       0   23   28   9
 1  220  214   4      -1   91   93   6      10   67   69   7       1  376  385   4
 2  419  420   5       0  121  110   5      11  140  136   5       2  492  484   5
 3  625  641   6       1  336  321   5      12  -31    4  11       3   87   81   4
 4  134  151   4       2  311  302   5                             4  445  454   4
 5  714  715   7       3   26   58  13          6   -5   1         5  491  485   5
 6  237  242   4       4   32   36  12                             6  484  475   5
 7  -12   47  18       5   -2   19  25       0   37   35   8       7  226  230   4
 8  -23   44  12       6  147  138   5       1  199  196   4       8  176  175   4
 9  -15   21  17                             2  142  141   4       9  261  257   4
10   75  102   6          5   16   1         3  248  245   4      10  -35    7   8
11  190  198   5                             4  197  194   4      11  -19    5  12
                       1  242  235   5       5  230  230   4      12  425  435   5
    5   12   1                                6   27   34  10      13  196  186   5
                          6  -10   1         7  179  182   4      14   22   16  15
-9   49   65   9                             8  272  268   4      15  129  120   5
-8  319  331   5       0   15   27  18       9  372  385   5
-7  270  258   5       1   87   83   6      10  300  290   4          6    0   1
-6  345  330   5       2   32   20  11      11   77   89   6
-5  228  235   4       3  133  127   5      12  -44    0   8     -11  120  109   5
-4  332  349   4       4  -44    7   8      13  -31   50  11     -10   44   57   9
-3  159  158   4       5  110  116   5                            -9   80   95   6
-2  -21    5  13       6  -15   43  17          6   -4   1       -8  114  113   5
-1  357  354   4       7   57   63   8                            -7   79   84   6
 0  175  192   4                             0  257  250   4     -6  196  189   4
 1  357  349   4          6   -9   1         1  223  218   4     -5  232  230   4
 2   78   81   5                             2   92   74   4     -4   40   30   7
 3  221  216   4       0  291  270   5       3  202  205   4     -3  232  242   4
 4   35   39   9       1  264  258   4       4  668  695   6     -2  245  249   3
 5   98  102   5       2   97   98   5       5  327  323   4     -1  187  179   3
 6  171  168   4       3   56   56   7       6  -31   11   8      0  214  206   3
 7  -50    0   6       4  160  154   5       7   79   87   4      1  229  226   3
 8   77   94   6       5  182  172   4       8   69   69   6      2  876  866   8
 9   -4   35  23       6  -22   14  13       9  443  434   5      3  103   85   3
10  174  163   5       7   44   59   9      10  440  447   5      4  102   85   3
                       8  124  115   5      11  272  278   4      5  112  104   3
    5   13   1         9   94  107   6      12   79   94   6      6  309  315   4
                                            13  142  144   5      7  141  134   4
-7  126  134   5          6   -8   1        14  -27   23  13      8   67   80   5
-6   18   23  16                                                  9  223  232   4
-5  262  248   4       0   99  100   5          6   -3   1       10  443  437   5
-4   50   61   7       1   59   58   7                           11  177  173   4
-3  265  268   4       2  -31    6  10       0  245  243   4     12  288  287   4
-2  447  440   5       3   85   91   5       1  198  201   3     13  268  268   5
-1  203  206   4       4   41   46   8       2   34   37   7     14  254  262   5
 0  365  363   5       5  168  162   4       3  118  124   4     15  -14   22  19
 1  193  199   4       6  236  237   4       4  112  118   4
 2   68   81   6       7   73   59   6       5  -11   22  15          6    1   1
 3  123  131   5       8  115  111   5       6  204  199   4
 4  281  287   4       9   92   68   6       7  125  135   4     -11  117  113   6
 5  -37   13   8      10  283  266   5       8  114  116   4     -10  106   92   6
 6  462  465   5                             9   62   72   6     -9  -27    9  12
 7  120  127   5          6   -7   1        10   48   56   8     -8  -28   50  11
 8   52   58   8                            11  124  122   5     -7   67   50   6
 9   70   79   7       0   76   74   6      12   39   35   9     -6  127  120   4
                       1  139  134   4      13   62   53   7     -5   27   22  10
    5   14   1         2   40   37   9      14  331  329   5     -4   83   82   5
                       3  143  151   4                           -3  109  116   4
-6   42   72   9       4  -34   21   9          6   -2   1       -2   85   65   4
-5  193  179   5       5   93   83   5                           -1  209  206   3
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Tetrakis(pentafluorophenyl)-beta-octachloroporphyrin

```
  0  521  535   5        -11   66   67   7         6   71   94   5         0  161  161   4
  1  231  240   3        -10   47   39   8         7  439  437   5         1  121  125   4
  2  691  710   6         -9   92   86   6         8   43   16   7         2  514  520   5
  3  117  107   3         -8  163  166   4         9  154  163   4         3   49   44   6
  4   45   28   4         -7   32   24  10        10  378  364   5         4  492  480   5
  5  135  141   3         -6  286  278   4        11  328  321   5         5   97   91   4
  6  103  103   4         -5   38   14   8        12  104   82   5         6  663  672   6
  7  512  498   5         -4  386  384   4        13   44   52   9         7  285  283   4
  8  589  595   6         -3  424  413   4        14  118  134   5         8  326  321   4
  9  263  252   4         -2  165  168   3                                 9  -31   28   8
 10  274  260   4         -1  169  164   3         6    7   1             10   68   74   6
 11  -32    5  10          0   88   90   4                                11  -40   24   8
 12  382  383   5          1  172  170   3        -11  117  101   6       12  244  237   5
 13  108   99   5          2  593  592   5        -10   38   37  11       13  304  303   5
 14  166  173   5          3  478  470   4         -9   64   81   7
 15  195  187   5          4  168  163   3         -8  297  304   4        6   10   1
                           5  160  152   3         -7  336  326   4
  6    2   1               6  340  330   4         -6  144  140   4        -9  -42    0   8
                           7  266  261   4         -5  153  153   4        -8   98  105   6
-11  -16   15  18          8  173  165   4         -4  271  271   4        -7   61   60   7
-10   64   64   7          9  119  127   4         -3  -25   17   9        -6  444  442   5
 -9  127  117   5         10  229  222   4         -2  357  369   4        -5  213  203   4
 -8  139  151   5         11  461  466   5         -1  403  396   4        -4   34   17  10
 -7  203  212   4         12  220  230   4          0  342  334   4        -3  381  382   4
 -6  453  452   5         13  290  283   4          1   82   74   4        -2  105   87   4
 -5  239  237   4         14  327  320   5          2  472  463   4        -1  333  325   4
 -4  100  103   4         15  214  220   5          3  282  278   4         0  168  167   4
 -3  269  274   4                                   4  245  228   3         1  221  225   4
 -2  311  299   4          6    5   1               5  447  433   5         2  191  194   4
 -1  918  902   8                                   6   43   40   7         3  184  179   4
  0  680  665   6        -11  153  145   5          7  129  129   4         4  344  350   4
  1   79   49   4        -10  -16   14  17          8  148  162   4         5  203  211   4
  2  350  327   4         -9  236  239   4          9  350  353   4         6  240  233   4
  3  237  225   3         -8  142  149   5         10  315  322   4         7  212  212   4
  4  471  451   5         -7  175  168   4         11    5    0  23         8  -31   20  10
  5   61   72   5         -6  190  188   4         12   61   60   7         9  130  121   5
  6  504  497   5         -5  205  212   4         13  250  248   5        10  209  209   4
  7  213  216   4         -4  113  111   4         14   39   42  11        11  -45   12   6
  8  148  158   4         -3  191  184   3                                12   52   61   9
  9  304  310   4         -2   30   10   8          6    8   1
 10  114   95   4         -1   60   29   5                                 6   11   1
 11   67   76   6          0   47   41   5        -10  119  115   5
 12  317  303   5          1  155  168   3         -9  102   89   5        -9   60   72   8
 13  223  220   4          2  257  248   3         -8  107   93   5        -8   90   70   6
 14   52   39   8          3  433  438   4         -7  559  554   6        -7   95   99   8
 15   36   22  11          4  256  238   3         -6  117  116   5        -6  124  116   5
                           5  277  270   4         -5  119  120   4        -5  374  381   5
  6    3   1               6  253  244   4         -4  228  227   4        -4  440  434   5
                           7  195  197   4         -3  122  128   4        -3  296  306   4
-11  -17   11  17          8  748  756   7         -2  568  572   5        -2  108  106   5
-10  127  132   5          9  298  306   4         -1   44    9   6        -1  -22   16  11
 -9  295  291   5         10   97  102   5          0  -24   12   9         0   26   31  11
 -8  130  130   5         11  253  257   4          1  365  360   4         1   23   21  11
 -7   48   32   8         12  208  213   4          2   26    4   9         2  552  545   5
 -6  234  229   4         13  161  153   5          3  200  202   3         3  308  320   4
 -5  431  440   5         14  214  205   5          4  351  363   4         4  121  106   4
 -4  259  270   4         15  -30   44  12          5  527  529   5         5   56   40   8
 -3  254  251   4                                   6  623  620   6         6  211  212   4
 -2   68   48   5          6    6   1               7   84   77   5         7  -19   58  14
 -1   52   21   4                                   8  187  189   4         8  354  360   5
  0  107  110   3        -11  112  114   6          9   73   77   6         9  -43   14   8
  1  453  441   3        -10   85   89   6         10   29   51  11        10  176  182   5
  2   49   31   5         -9  207  193   4         11  236  237   4        11   91   92   6
  3  492  483   5         -8   76   65   6         12  -27    4  12
  4  582  575   5         -7  223  213   4         13   97   90   6         6   12   1
  5  183  191   3         -6  129  135   4
  6  186  176   3         -5  124  128   4          6    9   1             -8  144  141   5
  7  349  339   4         -4  108  100   4                                -7  109  103   5
  8   94   90   4         -3  421  418   4        -10   43   45   9        -6   11   26  19
  9  318  316   4         -2  241  244   3         -9  -30   29  11        -5   51   33   8
 10  178  170   4         -1  158  161   3         -8  201  210   4        -4  207  195   4
 11  242  247   4          0  291  292   4         -7   87   69   5        -3   81   68   6
 12  361  353   5          1   57   60   5         -6   67   81   6        -2  193  180   4
 13   35   51  11          2  197  180   3         -5   51   58   7        -1  559  578   6
 14  171  164   5          3  576  567   5         -4  111  121   4         0  438  446   5
 15   30   48  11          4  411  421   4         -3  163  166   4         1  164  169   4
                           5   94   85   4         -2   68   72   5         2  177  170   4
  6    4   1                                       -1  314  322   4         3  118  118   4
```

Tetrakis(pentafluorophenyl)-beta-octachloroporphyrin   Page 18

```
  4  100  109   5
  5  134  144   4
  6  -40    0   8
  7   27   37  12
  8  180  162   4
  9  173  182   5
 10  252  216   5

      6  13  l

 -7   33   32  12
 -6   27   41  13
 -5  332  336   5
 -4  113  112   5
 -3   17   20  16
 -2  100  101   5
 -1   44   40   8
  0   98   85   5
  1   98  101   5
  2   62   64   7
  3   30   50  11
  4  202  209   4
  5   20   39  14
  6   47   57   8
  7  198  199   4
  8  114  112   5
  9  186  182   5

      6  14  l

 -5   59   46  10
 -4  215  228   5
 -3   73   69   6
 -2  148  147   5
 -1  229  228   4
  0  345  337   5
  1  201  213   4
  2   75   72   6
  3  -36    5   9
  4  137  146   5
  5  117  120   5
  6    7   23  23
  7  100   98   6

      6  15  l

 -3  169  150   5
 -2   47   40   9
 -1  352  355   5
  0  250  243   5
  1  106  119   5
  2  287  277   5
  3  109  115   5
  4  379  375   5
  5  142  143   5

      7  -9  l

  0   97   93   6
  1   59   42   8
  2   53   62   8
  3  216  213   5
  4   21   39  15
  5   24    4  13
  6   12   32  19

      7  -8  l

  0   62   55   6
  1   66   56   6
  2  133  150   5
  3   64   66   7
  4   59   85   7
  5  181  180   5
  6  165  168   5
  7  -20   20  15
  8   59   49   8
  9   50   42   9
```

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      7  -7  l

  0  174  166   4
  1   87   86   6
  2  110  124   5
  3   80  110   6
  4   57   47   7
  5  143  145   5
  6   52   58   8
  7  254  252   4
  8  112  118   5
  9   25   25  12
 10  150  142   5

      7  -6  l

  0  193  193   4
  1   50   37   8
  2   59   68   7
  3   67   86   6
  4   90   83   5
  5  133  115   4
  6   71   76   6
  7  245  248   4
  8  -17   30  14
  9  188  196   4
 10    3   40  26
 11  108  101   5

      7  -5  l

  0  205  206   4
  1   33   47  10
  2   -2   27  24
  3  105   96   5
  4   38   16   9
  5   61   58   6
  6  260  253   4
  7  128  119   4
  8  102  106   5
  9   64   28   7
 10  149  155   5
 11  -20   20  15
 12   76   73   7

      7  -4  l

  0   50   33   7
  1   89   98   5
  2   77   61   4
  3  339  350   4
  4   42   34   8
  5   61   56   6
  6  296  302   4
  7  101   96   5
  8  242  243   4
  9  263  269   4
 10  340  359   5
 11   47   64   9
 12  -17   29  14
 13  341  328   5

      7  -3  l

  0   95   88   4
  1   19   27  12
  2   32   15   9
  3  121   95   4
  4  508  514   5
  5  115  112   4
  6   33    1   9
  7   73   72   5
  8  272  274   4
  9  117  120   5
 10   93   93   5
 11  160  153   5
 12   29   39  12
```

```
 13  140  131   5

      7  -2  l

  0   47   61   7
  1   97  108   4
  2   66   76   5
  3  108  105   4
  4  237  240   4
  5  214  202   4
  6  -27   12   9
  7   69   72   5
  8  128  125   4
  9  218  220   4
 10  171  167   4
 11   24    8  12
 12  116  106   5
 13   22    5  15
 14  246  242   5

      7  -1  l

  0  106  108   4
  1  180  181   3
  2   35   43   7
  3   31   20   7
  4   65   63   5
  5   51   62   6
  6   -4   41  20
  7  239  246   4
  8  245  246   4
  9   32   46  10
 10  144  154   4
 11   73   65   6
 12  102  111   5
 13  127  128   5
 14  185  167   5

      7   0  l

 -9  101  100   6
 -8  127  148   5
 -7   27   19  13
 -6   42   46   9
 -5  159  161   4
 -4   32    4   9
 -3   48   51   6
 -2   62   78   5
 -1  118  110   4
  0   19    0  10
  1  327  327   4
  2   66   52   5
  3  192  191   3
  4  295  287   4
  5  234  223   4
  6  384  378   4
  7   42   25   7
  8  414  408   5
  9  290  296   4
 10  -15   52  15
 11  149  139   4
 12  253  264   4
 13   19   47  15
 14   23   29  15

      7   1  l

-10   42   24  10
 -9   61   87   8
 -8  108  127   5
 -7   30   45  12
 -6   64   60   7
 -5  130  130   4
 -4   17   16  14
 -3   61   74   6
 -2  135  141   4
 -1  341  342   4
  0  132  131   4
```

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  1   36   33   7
  2  121  120   3
  3  284  291   4
  4  106   93   4
  5  337  331   4
  6  243  250   4
  7  562  578   5
  8  204  202   4
  9  254  254   4
 10  381  373   5
 11  208  198   4
 12  137  148   5
 13  173  179   5
 14  118  100   5

      7   2  l

-10   71   74   7
 -9  -16   47  18
 -8   61   58   6
 -7   32   52  11
 -6   57   70   7
 -5   81   69   5
 -4  117  117   4
 -3  174  184   4
 -2  180  187   4
 -1   21   27   9
  0   69   54   5
  1   62   62   4
  2  120  119   3
  3   43   34   6
  4  320  316   4
  5  103   84   4
  6  330  331   4
  7  161  167   4
  8  140  132   4
  9   39   32   8
 10  292  304   4
 11  389  391   5
 12  278  286   4
 13  246  228   5
 14  125  145   5
 15  356  343   5

      7   3  l

-10  123  126   5
 -9   85   88   6
 -8   88   70   6
 -7  228  216   4
 -6  -18   13  15
 -5   81   83   5
 -4  327  319   4
 -3  305  307   4
 -2   30    4   9
 -1  276  261   4
  0  127  133   4
  1  221  218   4
  2   38   32   7
  3   27   33  10
  4  803  805   7
  5  252  235   4
  6  202  197   4
  7  380  377   4
  8  191  183   4
  9   33   29  10
 10  156  167   4
 11  336  343   5
 12   67   57   7
 13  125  126   5
 14   55    9  11
 15  170  168   5

      7   4  l

-10  -34   15  11
 -9   87   91   6
 -8  138  138   5
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Tetrakis(pentafluorophenyl)-beta-octachloroporphyrin

```
-7  201  191   4        7   7   1          12   87   94   6     0   94  114   5
-6  114  130   5                           13   28   46  12     1  178  162   4
-5  168  161   4      -10  102  117   6                         2  482  471   5
-4  126  123   4       -9  110  107   6      7  10   1          3   59   67   6
-3   98   94   4       -8   25   30  12                         4  107  126   5
-2   45   38   7       -7  102   84   5      -8  -26    1  13    5  -32   37  10
-1  251  236   4       -6   44   72   8      -7  129  133   5    6   77   99   6
 0  397  395   4       -5   38   34   9      -6  108   99   5    7  -25   29  13
 1  223  228   3       -4   12    5  16      -5   18   20  14    8   88   80   6
 2  168  164   3       -3  132  135   4      -4   50   41   8    9  -22    3  14
 3  136  146   3       -2  327  350   4      -3   39   60   9
 4   23   24  10       -1  217  210   4      -2  461  467   5    7  14   1
 5  570  556   5        0  213  219   4      -1  156  158   4
 6  341  343   4        1   42    2   7       0  127  143   4   -4  139  130   5
 7  169  157   4        2  475  469   5       1  -34   20   8   -3  190  190   5
 8  278  271   4        3  295  294   4       2   25   11  11   -2   50   22   8
 9  -25   13  11        4  220  225   4       3  679  687   6   -1   99  109   5
10  137  137   4        5   53   60   6       4  473  473   5    0  113  120   5
11   37   13   9        6  234  227   4       5  121  116   4    1  -12    2  19
12  245  250   4        7  113   88   4       6  427  417   5    2   93  103   6
13  -33   18  10        8  750  760   7       7  168  168   4    3  118  110   5
14  209  223   5        9  185  187   4       8  -39   32   8    4  242  246   5
                       10  -41    5   6       9  163  163   4    5   84   70   6
    7   5   1           11   52   72   8      10   88  106   6    6  335  324   5
                       12   30    5  12      11  113  121   5    7  243  225   5
-10   29   34  12       13  326  315   5      12   33    8  12
 -9  207  201   5       14  127  123   5                        7  15   1
 -8  124  116   5                             7  11   1
 -7  122  116   5        7   8   1                             -1   29   41  12
 -6  211  200   4                             -8  317  295   5   0   91   98   6
 -5   84   56   5       -9   59   60   8      -7   92   85   6    1   14   27  18
 -4   91   79   5       -8  171  175   5      -6  186  180   5    2  214  217   5
 -3   90   87   5       -7  185  201   4      -5  122  115   5    3  197  181   5
 -2  451  434   5       -6   90   80   5      -4   76   76   6    4  144  143   5
 -1  263  257   4       -5  217  207   4      -3  335  345   4
  0  348  347   4       -4  199  193   4      -2  370  363   5    8  -8   1
  1  631  641   6       -3  416  403   5      -1  175  170   4
  2  285  280   4       -2  259  267   4       0  155  151   4    2   92   93   6
  3  209  210   3       -1  152  161   4       1   33   26  10    3   55   32   7
  4   85   91   4        0  238  235   4       2  -31   15   9    4   60   52   7
  5  386  381   4        1  180  180   4       3  191  183   4
  6   37   44   7        2  600  605   6       4  157  160   4    8  -7   1
  7  550  564   5        3  277  283   4       5   96   92   5
  8  376  372   4        4  491  495   5       6   72   47   6    0  153  140   5
  9   47   56   8        5   72   51   5       7  294  296   4    1   48   52   9
 10   20    5  14        6  245  244   4       8  182  173   4    2   26   31  11
 11  539  537   6        7  298  316   4       9  261  270   4    3   84  107   6
 12   81   99   6        8   71   65   6      10   99  115   6    4   60   66   7
 13   38   38  10        9   92   85   5      11  284  268   5    5   66   73   7
 14   62   83   8       10   48   65   8                         6  167  160   5
                       11   98  111   5      7  12   1           7   76   84   6
    7   6   1           12   24   17  14                         8   51   66   9
                       13  133  129   5      -7   97   86   6
-10   33    5  12                            -6  123  131   5    8  -6   1
 -9  108  108   6        7   9   1           -5  -26    1  12
 -8   81  102   6                            -4  215  226   4    0  189  184   4
 -7  120  106   5       -9  137  139   5     -3  150  146   4    1  162  163   5
 -6  207  192   4       -8   79   84   5     -2  182  187   4    2   66   69   7
 -5   52   55   7       -7   90   91   6     -1  -30   13  10    3   17   18  16
 -4   64   74   6       -6  224  221   4      0  186  191   4    4  266  270   4
 -3  394  407   4       -5   32   21  10      1  496  499   5    5   76   81   6
 -2  114  117   4       -4  126  134   4      2  419  412   5    6   68   71   7
 -1  410  408   4       -3   43   19   7      3  -25    6  11    7   50   54   8
  0  299  287   4       -2  229  230   4      4  -50    9   6    8   82   84   6
  1   63   55   5       -1  125  109   4      5  -27    6  11    9   89   99   6
  2  454  452   5        0  200  195   4      6   76   86   6
  3  242  240   4        1  179  181   4      7  291  296   4    8  -5   1
  4  -22    1  10        2  423  423   5      8  139  136   5
  5  208  208   4        3   76   67   5      9  -34   20  10    0   44   33   7
  6  152  153   4        4  143  146   4     10   33   45  12    1   35    9  10
  7  292  296   4        5  446  447   5                        2  239  228   4
  8  452  451   5        6   54   40   7      7  13   1          3   51   27   8
  9  565  567   6        7  292  284   4                        4   52   23   8
 10  206  196   4        8  359  357   5     -5   73   65   6    5  109   89   5
 11  105  114   5        9   72   86   6     -4   91   78   6    6  109   90   5
 12  629  605   6       10  -42   11   8     -3   49   40   8    7   65   51   7
 13  120  119   5       11   30   39  12     -2   57   43   6    8  328  345   5
 14  -17   20  17                            -1  280  284   4    9  -24   26  13
```

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 10   40    8 10        -1  169  165  4        -3  341  342  4        -6  152  133  5
 11   13    6 19         0  106  109  4        -2  257  266  4        -5   85   82  6
                         1  268  267  4        -1   28   10 11        -4  109  112  5
   8  -4  1              2  157  165  4         0  301  284  4        -3  150  142  4
                         3   95   82  4         1  200  202  4        -2  113  111  4
  0   88   91  5         4  385  376  4         2   78   81  5        -1  133  127  4
  1   38   28  9         5  288  296  4         3  132  127  4         0   38   15  7
  2  325  325  4         6   39   29  7         4  120  124  4         1   47   38  7
  3  100  111  5         7  294  299  4         5  151  147  4         2   33    1  8
  4  399  395  5         8   87   86  5         6   70   88  6         3   51   13  6
  5  119  117  5         9  218  223  4         7  113  106  4         4  141  138  4
  6   93  100  5        10  133  126  5         8  124  121  4         5  124  135  4
  7  242  246  4        11  116  115  5         9   80   88  6         6  228  232  4
  8  233  220  4        12  256  243  5        10  -39   12  8         7  115   95  4
  9   37   14  9        13  107  107  6        11   90   89  6         8   71   59  5
 10   35   29 11        14   47   54 10        12   96  114  6         9   85   65  6
 11   82   85  6                               13  125  119  5        10   77   61  6
 12  144  132  5          8   1  1             14  144  148  5        11   27   14 13
                                                                      12   54   57  8
   8  -3  1             -8   41   62 10          8   4  1              13  139  144  5
                        -7   37   30 11
  0   64   49  6        -6   83   78  6        -9  108   96  6          8   7  1
  1  134  138  4        -5  356  354  5        -8    1   21 29
  2   37    6  9        -4   67   59  6        -7  110  111  5        -8   27    8 14
  3  199  194  4        -3  144  155  4        -6  184  190  4        -7   25   17 14
  4  165  155  4        -2  373  377  4        -5  138  133  5        -6  275  263  5
  5  192  191  4        -1  314  317  4        -4   45    9  9        -5  151  151  4
  6  -33    6  9         0   83   80  5        -3  285  271  4        -4   76   76  5
  7  145  142  4         1  117  121  4        -2  354  353  4        -3  252  255  4
  8  110  105  5         2  126  128  4        -1  197  197  4        -2  195  193  4
  9  361  337  5         3  377  382  4         0  307  308  4        -1  -12    3 16
 10   54   38  8         4   63   58  4         1   44    0  7         0  245  240  4
 11  180  195  5         5  128  119  4         2  308  308  4         1  111  101  4
 12   -8   32 23         6   88  103  5         3  586  590  6         2  152  153  4
                         7  115  111  4         4   68   51  5         3  164  173  4
   8  -2  1              8  194  190  4         5   85   74  5         4   38   44  8
                         9  130  135  5         6  158  165  4         5  274  258  4
  0  155  160  4        10  156  155  4         7   68   72  6         6  632  622  6
  1  137  161  4        11   76   64  6         8  212  208  4         7   41   35  8
  2  298  308  4        12  124  129  5         9  148  158  4         8  116  107  5
  3  139  114  4        13   49   47  9        10  220  226  4         9  412  406  5
  4   82   85  5        14   92   82  6        11  -24   25 13        10  106  118  5
  5   59   70  6                               12   34   38 10        11   33   39 11
  6   34   41  9          8   2  1             13  140  142  5        12  477  469  6
  7   54   51  7                               14   87   95  6        13  193  177  5
  8  212  219  4        -9  102  101  6
  9    8   10 21        -8   39   31 11          8   5  1              8   8  1
 10  431  424  5        -7  191  201  5
 11  148  157  5        -6  285  285  5        -9   51   69  8        -8  -11   16 21
 12  105  117  6        -5   68   42  6        -8   13   30 20        -7   51   67  9
 13   67   61  7        -4  134  133  5        -7   59   38  7        -6  110  111  5
                        -3  104   88  5        -6  110  114  5        -5   37   40  9
   8  -1  1             -2   80   70  5        -5   13   30 16        -4   43   55  8
                        -1  108  113  4        -4   29   34 11        -3  225  228  4
  0  204  206  4         0  233  230  4        -3  110  112  5        -2  378  377  5
  1  256  269  4         1   35    4  8        -2  203  207  4        -1  250  252  4
  2  264  270  4         2  136  135  4        -1   49   33  7         0  103   97  4
  3  351  361  4         3  175  173  4         0  135  143  4         1  129  125  4
  4   44    1  7         4   63   47  5         1  244  235  4         2   24   10 10
  5  189  188  4         5  224  221  4         2   49    7  5         3   86   99  5
  6   32   45  9         6  312  306  4         3  334  331  4         4  526  523  5
  7   65   65  6         7  192  193  4         4  391  386  4         5  255  244  4
  8  162  157  4         8  409  416  5         5  265  270  4         6  412  405  5
  9  141  142  4         9  118  120  5         6  -29    1  9         7  313  313  4
 10   74   86  6        10  111  131  5         7  149  147  4         8  359  360  5
 11  232  226  4        11  -15   16 17         8   46   30  7         9  103  100  5
 12   56   66  8        12  -11   15 18         9  252  241  4        10  144  150  5
 13  165  163  5        13  -22   22 15        10  390  371  5        11   80   84  6
                        14  354  326  5        11  367  366  5        12  261  270  5
   8   0  1                                    12   66   77  7        13  -26   24 13
                         8   3  1              13  245  242  5
 -8  116  113  6                               14  187  197  5          8   9  1
 -7   57   73  8        -9  159  147  5
 -6   81   78  6        -8   31   55 12          8   6  1             -8   82   65  7
 -5  128  113  5        -7  103   94  6                              -7  219  233  5
 -4   99  108  5        -6   67   58  6        -9   47   49 10        -6  171  189  5
 -3  139  153  4        -5   83   73  6        -8  120  132  5        -5  198  196  4
 -2   93   83  5        -4  169  154  4        -7  413  421  5        -4  164  154  4
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Tetrakis(pentafluorophenyl)-beta-octachloroporphyrin

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-3   91   89   5          -4   82   91   6          0  119  106   5          -7   36   32  11
-2   75   60   6          -3  176  160   5          1  409  430   5          -6  125  117   5
-1  209  214   4          -2   15    3  17          2   96   86   5          -5   57   45   8
 0   52   44   6          -1    8   30  21          3  206  216   4          -4  148  166   5
 1  233  229   4           0  122  122   5          4   59   52   7          -3  181  182   4
 2   33   27   9           1   65   47   7          5  104  112   5          -2  169  161   4
 3   52   32   7           2   67   51   6          6  211  225   4          -1   93   70   5
 4   34   12   9           3  305  300   5          7   26   43  10           0  115   99   4
 5   74   67   6           4   64   66   7          8  100   99   5           1  222  218   4
 6  278  291   4           5   50   59   8          9   50   55   8           2  374  364   4
 7  208  208   4           6   58   52   8         10   55   52   8           3  144  145   4
 8  500  511   5           7  375  368   5         11  125  110   5           4  197  197   4
 9  208  219   4           8  228  218   5                                    5   49   57   7
10   37   55  10                                    9  -1   1                 6  165  161   4
11   91   98   6           8  14   1                                         7  442  443   5
12   12   27  21                                    0  145  118   4           8   81   75   6
                          -2  177  161   5          1  241  246   4           9  -34    9  10
 8  10   1                -1    7    2  23          2  165  156   4          10  123  131   5
                           0  247  245   5          3   54   36   7          11  262  257   5
-7  134  113   5           1   69   83   7          4  182  179   4          12  -14   35  19
-6   68   76   6           2  267  263   5          5  260  252   4          13  281  275   5
-5  152  165   5           3  339  346   5          6   63   50   6
-4  146  136   5           4  -27   23  12          7  373  376   5           9   3   1
-3   82   98   6           5  189  177   5          8   95  100   5
-2  118  128   5           6  204  202   5          9   -8   33  22          -7  141  134   5
-1   -7    0  20                                   10   42   26   9          -6   74   77   7
 0  225  226   4           9  -6   1              11   32   44  12          -5    6    9  24
 1  156  157   4                                   12  266  267   5          -4  147  140   5
 2   52   44   6           1   79   68   6                                   -3   85   70   6
 3   72   61   6           2   40   40  10          9   0   1                -2   28    4  12
 4   45   13   8           3   28   18  13                                   -1   79   81   6
 5  311  299   4           4   86   81   6         -6   55   74   8           0  256  256   4
 6  157  147   4           5   41   26  10         -5   -5    0  24           1  216  215   4
 7  139  145   4           6  143  136   5         -4  -24    6  13           2   51   14   7
 8  -25    1  12                                   -3  194  189   4          3  272  283   4
 9  127  132   5           9  -5   1              -2   56    7   7           4  266  251   4
10  126  111   5                                   -1   98   49   5           5   25   35  12
11  294  290   5           0   84  101   6          0  114   78   5           6  118  109   5
                           1   39   43  10          1   76   36   6          7   23   11  14
 8  11   1                 2   19    5  15          2  125  116   4           8   38   25  10
                           3   14    2  16          3  105   88   5           9  -27    4  12
-6   55   61   8           4   91   86   6          4   36   10   9          10   44   38   9
-5  152  168   5           5  140  148   5          5   41   57   8          11   89   90   6
-4  103  102   5           6   82   95   6          6  246  261   4          12  261  248   5
-3  173  164   4           7   70   60   7          7   83   69   5          13  234  228   5
-2   33   37  10           8   51   53   8          8   57   66   6
-1   46   57   8                                    9  -16   18  15           9   4   1
 0   77   79   6           9  -4   1              10   25   13  14
 1  292  289   4                                   11  -12    9  20          -7   44   45   9
 2  101   86   5           0   40   21  10         12   39   48  11          -6  111  125   6
 3  352  349   5           1   44   23   9                                   -5  -19    9  16
 4  172  177   4           2  212  201   4          9   1   1                -4   81   77   6
 5   77   98   6           3   56   36   7                                   -3  206  198   4
 6  441  448   5           4   96  100   5         -7   30   14  13          -2   21    7  15
 7  301  306   5           5  145  151   5         -6   28   17  12          -1  148  133   4
 8  113  110   5           6   31    2  11         -5  182  175   5           0  141  100   4
 9  143  166   5           7   48   69   9         -4   69   66   7           1   58   12   7
10  265  263   5           8  172  163   5         -3  337  339   5           2  133  139   4
                           9   97   85   6         -2  110   71   5           3   82   62   5
 8  12   1                10   61   54   6         -1  291  299   4           4  281  287   4
                                                    0  164  159   4           5   53   43   7
-5   34    9  11           9  -3   1               1  292  300   4           6  153  153   4
-4  248  224   5                                    2  134  121   4           7  280  284   4
-3  117  123   5           0   80   78   5          3  149  163   4           8  104   99   5
-2   69   69   6           1  132  113   5          4  256  250   4           9   11   26  20
-1   89  108   6           2  171  160   4          5  168  171   4          10  288  298   5
 0   25   37  13           3  187  190   4          6  120  122   5          11   83   88   6
 1  308  311   4           4  104  121   5          7   28   22  11          12   55   38   8
 2  193  179   4           5   24    8  11          8  109   92   5          13  173  165   5
 3   23   21  13           6  -20   33  13          9  344  360   5
 4   98   90   5           7   27    4  12         10  105  124   5           9   5   1
 5  164  169   4           8   91   98   6         11  462  450   5
 6  137  150   5           9  -11    7  17         12  110  122   6          -7   88  104   6
 7   64   77   7          10   52   53   8         13   95   83   6          -6   79   68   7
 8   33   14  11          11   52   56   8                                   -5   95   87   6
 9  125  138   5                                    9   2   1                -4  179  183   5
                           9  -2   1                                         -3  280  281   4
 8  13   1                                                                   -2   42   28   9
```

Tetrakis(pentafluorophenyl)-beta-octachloroporphyrin

-1	207	209	4	8	275	279	4	**9**	**13**	**1**		7	292	286	5
0	157	164	4	9	52	32	8	-2	61	64	8	8	106	106	5
1	128	114	4	10	141	151	5	-1	174	173	5	9	82	72	6
2	338	339	4	11	-24	31	14	0	172	165	5	10	163	164	5
3	42	6	8	12	90	85	6	1	75	71	6	11	82	81	6
4	78	75	5					2	27	18	13				
5	131	141	4	**9**	**9**	**1**		3	85	86	6	**10**	**1**	**1**	
6	-19	28	14					4	-21	33	13				
7	106	123	5	-6	55	65	7	5	152	165	5	-4	94	107	6
8	32	0	11	-5	57	51	8	6	199	202	5	-3	76	52	6
9	330	326	5	-4	40	36	8					-2	72	74	6
10	-26	35	13	-3	116	130	5	**9**	**14**	**1**		-1	218	235	4
11	189	176	5	-2	302	309	4					0	286	292	4
12	67	63	7	-1	37	30	9	2	28	9	13	1	335	348	5
13	139	133	5	0	16	10	16	3	64	59	7	2	183	186	4
				1	107	106	5					3	72	86	6
9	**6**	**1**		2	97	97	5	**10**	**-4**	**1**		4	71	71	5
				3	487	487	5					5	90	73	5
-7	46	45	8	4	230	232	4	2	-36	8	9	6	53	51	8
-6	-37	4	10	5	179	173	4	3	66	51	7	7	208	204	4
-5	39	21	10	6	54	44	7	4	52	70	8	8	67	72	7
-4	156	154	5	7	100	72	5	5	61	50	7	9	38	53	10
-3	83	73	6	8	291	283	5	6	55	37	7	10	219	216	5
-2	266	268	4	9	260	265	5					11	70	56	6
-1	104	86	5	10	121	127	5	**10**	**-3**	**1**					
0	39	45	9	11	206	194	5					**10**	**2**	**1**	
1	57	58	6					0	-9	36	21				
2	77	76	5	**9**	**10**	**1**		1	45	43	8	-5	51	46	9
3	91	91	5					2	56	66	8	-4	168	146	5
4	134	127	4	-5	-30	3	11	3	128	112	5	-3	61	38	7
5	150	149	4	-4	86	102	6	4	134	131	5	-2	160	162	5
6	200	182	4	-3	78	74	6	5	116	121	5	-1	121	116	5
7	364	361	5	-2	21	5	13	6	86	111	6	0	62	48	7
8	553	555	6	-1	122	117	5	7	33	41	11	1	163	151	4
9	191	186	4	0	30	28	9	8	54	13	7	2	286	286	4
10	213	211	5	1	206	211	4					3	310	305	4
11	48	44	9	2	195	183	4	**10**	**-2**	**1**		4	84	81	5
12	158	166	5	3	490	501	5					5	40	28	9
				4	149	123	4	0	-21	27	14	6	204	205	4
9	**7**	**1**		5	287	303	4	1	12	31	19	7	105	91	5
				6	95	100	5	2	27	9	12	8	84	78	6
-7	84	80	7	7	82	97	6	3	54	27	8	9	147	137	5
-6	29	37	13	8	22	9	14	4	146	131	5	10	39	25	11
-5	194	187	5	9	-1	33	28	5	219	219	4	11	85	80	6
-4	63	72	7	10	178	170	5	6	44	30	9				
-3	264	274	4					7	116	112	5	**10**	**3**	**1**	
-2	59	34	6	**9**	**11**	**1**		8	120	128	5				
-1	310	301	4					9	94	87	6	-5	100	85	6
0	113	109	5	-5	134	131	5					-4	58	53	8
1	114	98	4	-4	123	127	5	**10**	**-1**	**1**		-3	118	101	5
2	17	4	15	-3	292	295	5					-2	80	81	6
3	114	123	4	-2	313	300	5	0	46	3	9	-1	29	7	12
4	66	72	6	-1	-31	15	10	1	117	138	5	0	187	175	4
5	29	30	11	0	271	270	4	2	177	174	4	1	313	312	4
6	105	85	5	1	164	163	4	3	94	69	5	2	133	107	4
7	159	160	4	2	227	214	4	4	31	15	11	3	118	129	5
8	67	72	7	3	48	68	8	5	43	21	9	4	90	85	5
9	290	285	5	4	242	254	4	6	29	12	12	5	207	220	4
10	105	115	5	5	316	318	5	7	131	141	5	6	57	57	7
11	63	57	8	6	289	289	5	8	78	76	6	7	153	160	5
12	56	9	8	7	66	62	6	9	26	19	14	8	110	108	5
				8	132	138	5	10	-40	5	9	9	-6	18	24
9	**8**	**1**		9	19	0	16					10	181	188	5
								10	**0**	**1**		11	55	56	9
-6	13	9	20	**9**	**12**	**1**						12	-15	38	19
-5	58	32	8					-4	60	31	8				
-4	51	51	8	-3	48	46	9	-3	38	64	11	**10**	**4**	**1**	
-3	46	25	8	-2	62	41	7	-2	33	39	11				
-2	72	38	6	-1	170	171	5	-1	51	19	8	-5	58	62	8
-1	178	181	4	0	58	50	7	0	89	54	5	-4	118	135	5
0	66	58	6	1	151	148	5	1	168	181	4	-3	90	88	6
1	262	274	4	2	84	90	6	2	63	62	7	-2	42	15	10
2	214	220	4	3	21	28	12	3	76	57	6	-1	72	72	7
3	43	19	8	4	49	61	8	4	55	54	7	0	49	48	8
4	16	1	14	5	-28	25	9	5	104	93	5	1	191	186	4
5	16	7	15	6	24	2	14	6	128	138	5	2	138	114	4
6	48	43	8	7	103	110	5					3	305	300	5
7	196	198	4	8	117	120	5					4	148	140	5

Tetrakis(pentafluorophenyl)-beta-octachloroporphyrin   Page 23

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  5   87   76   6        2   70   60   5       11   0   1          -2   52   60   9
  6  122  125   5        3  350  356   5                          -1   34   38  12
  7  137  111   5        4  165  154   4        0   43   11   8     0   88   79   6
  8   84   83   6        5  221  228   4        1   32   47  10     1   43   20   8
  9   96  100   6        6  144  135   5        2   72   62   7     2  149  158   5
 10  -20   14  15        7  110  108   5        3   54   63   7     3   71   59   7
 11  188  196   5        8   47   48   7        4  165  158   5     4   76   49   6
 12   75   87   7        9  -18   16  16        5   26   40  13     5   64   38   7
                        10  -18   12  17        6  135  123   5     6  154  135   5
 10   5   1                                     7   56   45   8     7  103   98   6
                        10   9   1              8  122  112   5     8  106  106   6
 -5   73   99   7                                                   9  124  122   6
 -4  -31    6  12       -4  111  126   5       11   1   1          10  -23   25  15
 -3   21    9  16       -3   40   22  10
 -2  193  157   5       -2   90   84   6       -1   84   83   6    11   6   1
 -1   35   33  11       -1   90   77   6        0   89   17   6
  0   94  101   5        0   46    5   8        1   54   44   8    -3  117  122   6
  1   47   37   8        1  112  122   5        2   62   43   7    -2  160  149   5
  2   51   41   7        2  329  330   5        3   87   89   6    -1   74   87   7
  3  101   78   5        3   60   47   6        4  194  189   5     0   37   37   9
  4  175  161   4        4   42   13   9        5   40   16  10     1   33   35  11
  5   72   65   6        5  127  127   5        6   96   93   6     2   64   55   7
  6  312  309   5        6   68   73   7        7   37   12  10     3  103   77   5
  7  186  182   5        7   47   47   9        8  104   96   6     4   64   41   7
  8  186  191   5        8  202  200   5        9   45   28  10     5  101   98   5
  9   84   88   6        9  143  153   5                           6  347  357   5
 10  196  197   5       10   78   70   7       11   2   1          7   72   71   7
 11   29   42  13                                                  8   32   31  12
                        10  10   1            -2  119  111   5     9   77   89   7
 10   6   1                                    -1   46   43   9
                        -3   80   85   6        0   36   35  11    11   7   1
 -5   26   52  13       -2  106  101   5        1  -21    0  14
 -4  106  115   6       -1  226  226   4        2  142  116   5    -2   42   29   9
 -3   91   75   6        0   42   38   9        3   96   78   5    -1   36   37  11
 -2   55   44   7        1   80  105   6        4   47   36   9     0   21   57  13
 -1   90   89   6        2  117  115   5        5   37   30  10     1   30   27  12
  0  128  129   5        3   82   83   6        6   64   79   7     2   34   24  11
  1  239  256   4        4  248  253   4        7  -12   44  20     3   61   31   7
  2   32   31  10        5   76   85   6        8   30   24  12     4  119  124   5
  3  259  250   4        6   55   41   8        9  100   84   6     5   58   42   8
  4  258  254   4        7  483  454   6                           6  157  143   5
  5   48    5   8        8   97   90   6       11   3   1          7   56   31   7
  6  233  226   4        9  189  186   5                           8   46   54  10
  7  120  120   5                              -2   60   49   7     9  -10   27  21
  8   90   96   6       10  11   1             -1   27   30  13
  9  145  152   5                               0   32    1  12    11   8   1
 10    9   13  22       -2   88   66   6        1  186  169   5
 11  258  256   5       -1  -20   11  13        2   90   86   6    -2  110   85   6
                        0   70   47   7         3  112  119   5    -1   47   42   8
 10   7   1             1  172  169   5         4   72   55   6     0   82   88   6
                        2  193  198   5         5  -18    1  16     1   72   86   7
 -5   25   32  14       3   10    8  20         6  107  101   5     2   78   70   6
 -4   38   43  11       4   -6   18  23         7  116  116   5     3  240  243   4
 -3  121  114   5       5   50   51   8         8  208  205   5     4   68   66   6
 -2  277  279   5       6  236  238   5         9   42   23   9     5  175  171   5
 -1  115  110   5       7  163  161   5        10   25   26  15     6   41   51  10
  0  119  114   5       8  203  196   5                            7  160  145   5
  1  114  111   5                              11   4   1          8   66   64   7
  2  288  279   4       10  12   1
  3  175  165   4                              -3  204  216   5    11   9   1
  4   58   10   7       -1   44   47   9       -2  230  231   5
  5  346  351   5        0  244  256   5       -1  193  191   5    -1  -14   14  18
  6   85   84   6        1   36   17  11        0   81   76   7     0  157  137   5
  7   61   10   7        2  135  123   5        1  155  150   5     1   51   66   8
  8  286  291   5        3  109   91   5        2   55   43   8     2  106  102   5
  9  -16   29  17        4  -20   15  13        3   61   43   7     3  -24    7  13
 10   39   39  11        5   64   66   7        4  154  154   7     4   -3    8  26
 11  230  224   5        6  103  102   6        5   78   89   7     5   77   70   6
                                               6   35   41  10     6   61   23   7
 10   8   1            11  -1   1              7   56   85   8     7   68   30   7
                                               8  -16    4  18     8   92   99   6
 -5   69   66   6        1   65   51   7        9  131  137   5
 -4   56   13   8        2  117  120   5       10   69   53   8    11  10   1
 -3   36    2  11        3   78   72   6
 -2   59   51   7        4  240  255   5       11   5   1          0   86   98   6
 -1   68   36   6        5   72   79   7                           1   59   56   8
  0  142  154   5        6   73   75   7       -3   88   62   7     2   -6   27  24
  1  110   92   5        7   76   36   7                           3   20    0  13
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Tetrakis(pentafluorophenyl)-beta-octachloroporphyrin

4	20	5	15	3	44	41	9	12	5	1		4	222	228	5
5	130	132	5	4	94	91	6					5	139	125	5
6	49	21	9	5	39	1	10	2	25	17	15	6	-6	3	25
								3	83	90	7				
11	11	1		12	4	1		4	39	19	12	12	7	1	
								5	182	185	5				
2	138	132	5	2	68	82	7	6	110	118	6	3	152	154	5
3	25	10	14	3	59	14	7					4	108	93	8
4	30	42	12	4	50	51	8	12	6	1		5	86	74	6
				5	29	29	13								
12	3	1		6	13	5	17	2	62	53	7				
								3	180	163	5				

Table 1. Final Heavy Atom Parameters for

Tetrakis(pentafluorophenyl)octachloroporphinato Zinc(II) $\cdot$ 6($C_6H_4Cl_2$).

x, y, z and $U_{eq}{}^a \times 10^4$

Atom	x	y	z	U_{eq} or B	Pop[†]
Zn	0	0	0	291(4)	
N	1015(4)	231(4)	95(9)	268(20)	
C1	2135(5)	108(6)	626(10)	286(26)	
C2	1542(5)	−246(5)	180(10)	297(26)	
C3	1475(5)	−943(5)	−120(11)	264(25)	
C4	1296(6)	861(6)	338(10)	287(28)	
C5	1989(6)	776(6)	720(10)	326(28)	
Cl1	2909(2)	−235(2)	1075(3)	484(8)	
Cl2	2544(2)	1359(2)	1352(3)	506(9)	
C6	2123(5)	−1340(6)	−259(11)	325(30)	
C7	2322(6)	−1829(6)	564(11)	346(29)	
F7	1935(4)	−1938(4)	1575(7)	547(20)	
C8	2900(7)	−2243(7)	393(14)	524(39)	
F8	3050(4)	−2723(4)	1207(8)	714(24)	
C9	3288(7)	−2138(8)	−611(14)	513(39)	
F9	3850(4)	−2525(5)	−810(8)	767(27)	
C10	3140(6)	−1612(7)	−1458(14)	533(41)	
F10	3529(4)	−1512(5)	−2431(8)	743(25)	
C11	2554(6)	−1232(5)	−1240(12)	329(28)	
F11	2406(4)	−770(4)	−2088(7)	549(20)	

Table 1. (Cont.)

Atom	x	y	z	U_{eq} or	B	Pop[†]
Cl3	4428(9)	6030(8)	1705(11)	1957(66)		0.50
Cl4	3904(6)	4528(8)	1753(12)	1411(45)		0.50
Cl5	5339(3)	910(4)	74(9)	2172(35)		
Cl6	4712(11)	1149(11)	2927(13)	2586(92)		0.47
Cl7	4300(10)	2220(11)	−277(23)	3762(115)		0.53
C31	4769	1516	620	1226		0.47
C32	4520	1628	1741	1229		0.47
C33	4060	2202	1935	1230		0.47
C34	3895	2612	964	1226		0.47
C35	4159	2490	−201	1229		0.47
C36	4608	1930	−396	1230		0.47
C41	4845	1295	1233	1225		0.53
C42	4449	1874	964	1229		0.53
C43	4104	2128	2010	1230		0.53
C44	4173	1816	3130	1225		0.53
C45	4602	1219	3265	1229		0.53
C46	4933	976	2264	1230		0.53
C14	5068	5371	1677	3.5	*	0.75
C15	4797	4709	1695	3.5	*	0.75
C16	5239	4163	1670	3.5	*	0.75

Table 1. (Cont.)

Atom	x	y	z	U_{eq} or$B$		Pop[†]
C17	5961	4262	1626	3.5	*	0.75
C18	6215	4923	1609	3.5	*	0.75
C19	5773	5469	1634	3.5	*	0.75
C21	4657	5072	1727	3.5	*	0.25
C22	4555	5782	1716	3.5	*	0.25
C23	5106	6237	1726	3.5	*	0.25
C24	5775	5977	1746	3.5	*	0.25
C25	5863	5255	1756	3.5	*	0.25
C26	5311	4818	1746	3.5	*	0.25

[a] $U_{eq} = \frac{1}{3} \sum_i \sum_j [U_{ij}(a_i^* a_j^*)(\vec{a}_i \cdot \vec{a}_j)]$

* Isotropic displacement parameter, B

[†] Population Parameter, if different from 1.0

Table 2. Anisotropic Displacement Parameters for
Tetrakis(pentafluorophenyl)octachloroporphinato Zinc(II) · 6(C$_6$H$_4$Cl$_2$).

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zn	246(8)	246(8)	381(15)	0	0	0
N	262(45)	193(44)	348(55)	−13(38)	−37(47)	31(47)
C1	265(59)	302(70)	290(62)	30(52)	−71(51)	−5(53)
C2	214(54)	337(62)	341(72)	12(47)	82(54)	104(56)
C3	299(61)	255(59)	239(64)	55(49)	52(58)	46(55)
C4	337(68)	274(64)	251(71)	−58(52)	−36(51)	−9(51)
C5	317(68)	269(63)	393(72)	−40(56)	−23(58)	−8(56)
Cl1	325(17)	409(18)	719(23)	64(14)	−208(17)	−66(17)
Cl2	378(18)	370(18)	769(25)	10(15)	−259(19)	−79(18)
C6	181(55)	290(61)	503(85)	31(48)	30(57)	−65(59)
C7	336(69)	372(70)	329(71)	42(58)	−33(58)	−11(59)
F7	509(48)	603(51)	529(45)	31(38)	27(41)	112(41)
C8	469(86)	385(80)	718(113)	121(71)	−235(82)	−134(74)
F8	797(59)	461(48)	885(65)	288(45)	−309(53)	66(47)
C9	315(74)	569(97)	654(99)	161(72)	−90(74)	−204(84)
F9	407(46)	766(60)	1128(75)	328(45)	−143(46)	−271(57)
C10	272(71)	624(94)	702(109)	−27(69)	196(75)	−262(88)
F10	529(52)	879(64)	822(59)	−3(45)	305(50)	−253(54)
C11	272(63)	260(63)	455(74)	−66(53)	−46(63)	−31(60)
F11	586(50)	543(48)	519(48)	−5(43)	156(41)	18(42)
Cl3	3244(222)	1771(143)	855(85)	799(149)	664(122)	−94(89)
Cl4	901(81)	2158(150)	1174(90)	−365(93)	261(71)	−130(98)
Cl5	1313(57)	1979(76)	3224(114)	−271(55)	510(69)	−1399(84)
Cl6	3216(276)	3402(265)	1139(111)	−2200(230)	−667(138)	947(142)
Cl7	2496(199)	3595(275)	5194(352)	−1801(195)	−2386(228)	3455(273)
C31	1002	925	1751	260	5	−205
C32	1368	1214	1105	−116	−302	437
C33	1272	1561	857	−193	286	−264
C34	1002	925	1751	260	5	−205
C35	1368	1214	1105	−116	−302	437
C36	1272	1561	857	−193	286	−264

Table 2. (Cont.)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C41	1156	1426	1093	−67	334	−410
C42	1426	1368	893	−222	−200	377
C43	1060	867	1763	250	−162	16
C44	1156	1426	1093	−67	334	−410
C45	1426	1368	893	−222	−200	377
C46	1060	867	1763	250	−162	16

$U_{i,j}$ values have been multiplied by 10^4

The form of the displacement factor is:

$$\exp -2\pi^2(U_{11}h^2a^{*^2} + U_{22}k^2b^{*^2} + U_{33}\ell^2c^{*^2} + 2U_{12}hka^*b^* + 2U_{13}h\ell a^*c^* + 2U_{23}k\ell b^*c^*)$$

Table 3. Complete Distances and Angles for
Tetrakis(pentafluorophenyl)octachloroporphinato Zinc(II) · 6(C$_6$H$_4$Cl$_2$).

		Distance(Å)			Distance(Å)
Zn	–N	2.032	C23	–C24	1.401
N	–C2	1.390(13)	C24	–C25	1.419
N	–C4	1.371(14)	C25	–C26	1.373
C1	–C2	1.431(15)	Cl5	–C31	1.728
C1	–C5	1.337(15)	Cl5	–C41	1.758
C1	–Cl1	1.722(11)	Cl6	–C32	1.640
C2	–C3	1.405(15)	Cl7	–C42	1.541
C3	–C6	1.490(15)	C31	–C32	1.334
C3	–C4	1.401(16)	C31	–C36	1.407
C4	–C5	1.423(16)	C32	–C33	1.449
C5	–Cl2	1.716(12)	C33	–C34	1.367
C6	–C7	1.365(16)	C34	–C35	1.393
C6	–C11	1.378(16)	C35	–C36	1.416
C7	–F7	1.354(14)	C41	–C42	1.399
C7	–C8	1.399(18)	C41	–C46	1.297
C8	–F8	1.324(16)	C42	–C43	1.415
C8	–C9	1.35(2)	C43	–C44	1.372
C9	–F9	1.349(17)	C44	–C45	1.441
C9	–C10	1.41(2)	C45	–C46	1.355
C10	–F10	1.320(16)			
C10	–C11	1.381(18)			
C11	–F11	1.324(14)			
Cl3	–C14	1.792			
Cl3	–C26	1.732			
Cl4	–C15	1.779			
Cl4	–C21	1.813			
C14	–C15	1.395			
C14	–C19	1.389			
C15	–C16	1.370			
C16	–C17	1.422			
C17	–C18	1.381			
C18	–C19	1.370			
C21	–C22	1.398			
C21	–C26	1.368			
C22	–C23	1.394			

Table 3. (Cont.)

			Angle(°)			Angle(°)
N	–Zn	–N	90.2	C10 –C11 –C6		123.8(11)
N	–Zn	–N	174.1	F11 –C11 –C6		121.0(10)
Zn	–N	–C2	125.2	F11 –C11 –C10		115.2(11)
Zn	–N	–C4	42.4	C15 –C14 –Cl3		113.5
C4	–N	–C2	106.9(8)	C19 –C14 –Cl3		126.2
C5	–C1	–C2	108.8(10)	C19 –C14 –C15		120.2
Cl1	–C1	–C2	128.2(8)	C14 –C15 –Cl4		123.8
Cl1	–C1	–C5	122.9(9)	C16 –C15 –Cl4		117.5
C1	–C2	–N	107.4(9)	C16 –C15 –C14		118.7
C3	–C2	–N	124.2(9)	C17 –C16 –C15		121.2
C3	–C2	–C1	128.4(10)	C18 –C17 –C16		118.8
C6	–C3	–C2	116.5(9)	C19 –C18 –C17		120.0
C4	–C3	–C2	126.5(10)	C18 –C19 –C14		121.1
C4	–C3	–C6	116.9(10)	C22 –C21 –Cl4		117.6
C3	–C4	–N	122.4(10)	C26 –C21 –Cl4		122.9
C5	–C4	–N	109.4(9)	C26 –C21 –C22		119.5
C5	–C4	–C3	128.0(10)	C23 –C22 –C21		121.3
C4	–C5	–C1	107.1(10)	C24 –C23 –C22		119.1
Cl2	–C5	–C1	122.9(9)	C25 –C24 –C23		118.3
Cl2	–C5	–C4	129.7(9)	C26 –C25 –C24		121.3
C7	–C6	–C3	122.5(10)	C21 –C26 –Cl3		128.3
C11	–C6	–C3	121.2(10)	C25 –C26 –Cl3		111.2
C11	–C6	–C7	116.4(11)	C25 –C26 –C21		120.4
F7	–C7	–C6	119.2(10)	C32 –C31 –Cl5		131.5
C8	–C7	–C6	123.0(11)	C36 –C31 –Cl5		105.3
C8	–C7	–F7	117.8(11)	C36 –C31 –C32		123.2
F8	–C8	–C7	119.8(12)	C31 –C32 –Cl6		123.2
C9	–C8	–C7	118.2(13)	C33 –C32 –Cl6		117.8
C9	–C8	–F8	121.9(13)	C33 –C32 –C31		119.1
F9	–C9	–C8	120.1(13)	C34 –C33 –C32		119.0
C10	–C9	–C8	121.9(13)	C35 –C34 –C33		121.4
C10	–C9	–F9	118.0(12)	C36 –C35 –C34		119.8
F10	–C10	–C9	121.1(12)	C35 –C36 –C31		117.5
C11	–C10	–C9	116.5(12)	C42 –C41 –Cl5		119.7
C11	–C10	–F10	122.3(12)	C46 –C41 –Cl5		110.3

Table 3. (Cont.)

Angle(°)

C46 –C41 –C42	129.9
C41 –C42 –Cl7	129.9
C43 –C42 –Cl7	117.8
C43 –C42 –C41	112.1
C44 –C43 –C42	121.2
C45 –C44 –C43	120.4
C46 –C45 –C44	118.5
C45 –C46 –C41	118.0

Table 4. Intermolecular Distances Less Than 3.5 Å for
Tetrakis(pentafluorophenyl)octachloroporphinato Zinc(II) · 6(C$_6$H$_4$Cl$_2$).

	Distance(Å)		Distance(Å)
C2 –Cl4	3.487(17)	C24 –C34	2.952
C4 –C17	3.387		
Cl1 –F10	3.122(9)		
Cl2 –C33	3.441		
Cl2 –C43	3.467		
Cl2 –F8	3.413(9)		
C7 –F10	3.234(15)		
F7 –C24	3.463		
F7 –C33	3.038		
F7 –C34	3.257		
F7 –C43	3.133		
F7 –C44	3.268		
F7 –F9	3.408(11)		
F7 –F10	3.344(11)		
C8 –F10	3.038(16)		
F8 –C34	3.401		
F8 –C35	3.199		
F8 –C10	3.125(16)		
F8 –F10	2.985(12)		
F8 –C11	3.165(14)		
F8 –F11	2.970(11)		
F9 –C24	3.485		
F9 –Cl4	3.168(15)		
F9 –C36	3.254		
F10 –C46	3.244		
F11 –Cl6	3.49(2)		
F11 –C32	3.336		
F11 –C44	3.473		
F11 –Cl3	3.014(17)		
F11 –C22	3.484		
F11 –C23	3.128		
C17 –C35	3.404		
C18 –C35	3.311		
C23 –C33	3.460		
C23 –C34	3.087		

Table 5. Observed and Calculated Structure Factors for

Tetrakis(pentafluorophenyl)octachloroporphinato Zinc(II) · 6(C$_6$H$_4$Cl$_2$).

The columns contain, in order, h, $10F_{obs}$, $10F_{calc}$ and $10\sigma F_{obs}$. A minus sign preceding F_{obs} indicates that F_{obs}^2 is negative.

Tetrakis(C6F5)-Octachloroporphinato Zinc 6(C6H4Cl2)   Page   1

```
  h   0    0            13   445   457  11      9   292   356  10     13   -69    98  31
                        14   372   365  12     10   315   308  11     14   377   325  14
  2   221   238   5     15   176   189  16     11   336   330  11     15    50   115  36
  4  1480  1421  13     16   157   141  18     12    26    63  45     16   276   291  13
  6   504   483   8     17   341   323  13     13   142   193  18     17   249   255  16
  8  1446  1447  14     18   274   273  15     14   143   121  19     18   210   175  14
 10   845   796  11     19   240   163  14     15   211   188  15     19   120   114  24
 12    46    65  31     20   181   153  17     16   564   480  13
 14   197   298  14     21   174   160  18     17  -106    16  22      h  13    0
 16  -115    48  17     22   -30    40  50     18   285   315  13
 18   487   566  13                            19   217   252  15     13   186    40  25
 20   237   146  14      h   4    0            20    97    43  26     14   144   187  18
 22    94   102  27                            21   183   160  18     15   107   133  23
                         4  2581  2483  26     22   -43    26  44     16   180   177  17
  h   1    0             5   670   620   8                           17   131   103  21
                         6   665   753   9      h   8    0            18    10   104  65
  1   935   921  10      7   600   625   9                           19   144   183  21
  2   749   904   7      8    75    80  20      8  1230  1226  17
  3  1185  1178  11      9   104   172  16      9   972   949  12      h  14    0
  4  1176   986  11     10  1814  1844  17     10    38    41  36
  5   506   423   7     11   133   227  15     11    20    86  48     14   -97    10  30
  6   368   422   7     12   591   598  11     12   261   279  13     15   -77    61  28
  7   380   446   8     13    56    30  31     13   943   904  13     16   124    56  22
  8   714   754   9     14   805   822  12     14   252   221  14     17   140   105  21
  9   822   768  10     15   258   226  14     15    21    31  55     18   -93    18  25
 10    71    55  22     16   102   148  24     16   454   398  13
 11   481   618  10     17   -37   111  45     17   -35     4  42      h  15    0
 12   712   783  11     18   450   433  13     18   -30    40  47
 13   231   315  12     19   314   241  12     19    57   100  36     15   461   424  17
 14   245   203  13     20   -56   133  35     20   293   284  14     16   292   288  14
 15   192   155  15     21   135   113  21     21    92    24  28     17   -64    34  34
 16   -88     2  23     22   213   203  16
 17   360   249  13                             h   9    0             h  16    0
 18    88   110  29      h   5    0
 19   121    64  20                             9   107    22  26     16   412   433  18
 20   221   191  15      5  1191  1145  15     10   291   238  12
 21   237   222  15      6  1467  1486  14     11   419   309  11      h   0    1
 22   141   137  21      7   460   453   9     12   -98    41  20
 23    25    91  56      8  1066  1029  12     13   352   301  12      1  1588  1641  12
                         9   494   501   9     14    53    47  36      2    48    41  13
  h   2    0            10   156   116  13     15   484   503  13      3  1174  1085   9
                        11   509   469  10     16   -82   132  28      4   581   561   6
  2   830   891  10     12   363   374  11     17   193   199  15      5   531   534   6
  3   464   452   6     13   199   236  14     18   166   141  18      6   496   500   6
  4   659   625   7     14   128   165  19     19   225   204  15      7  1182  1156  10
  5   437   456   7     15   345   337  12     20   206   178  16      8   485   495   6
  6   244   290   8     16   -28   183  48     21   198   152  17      9   692   687   7
  7   -54    31  21     17   603   567  13                           10   404   399   7
  8   591   611   9     18    64    25  36      h  10    0            11   499   494   7
  9   276   254   9     19   124    83  21                           12    72    92  17
 10   573   637   9     20   156   160  19     10   425   438  16     13   686   644   8
 11    48    67  29     21   479   413  12     11   478   509  11     14   -60    48  22
 12   344   317  10     22   214   180  16     12   145   139  18     15   496   440   8
 13   -65    97  25                            13   150   121  19     16   -84    35  17
 14   110   189  21      h   6    0            14   214   205  16     17   291   248  10
 15   593   652  12                            15   447   477  13     18   121   107  17
 16   141   176  19      6   570   647  12     16   -41    54  39     19   131    90  14
 17   232   123  15      7   -69    11  19     17   101    90  24     20   213   227  11
 18   546   505  13      8   112   109  16     18   211   189  15     21   121   153  16
 19   117   171  21      9   367   280  10     19   -90    98  25     22   193   221  12
 20   629   582  12     10   640   638  10     20  -116    12  20     23   148   126  15
 21    67    11  33     11   350   301  11
 22   102    70  26     12   493   473  11      h  11    0             h   1    1
 23   -85     2  28     13   421   414  11
                        14   402   342  12     11   145   251  26      2   379   384   4
  h   3    0            15   238   244  14     12   -38    84  42      3   880   808   7
                        16   207   206  16     13   477   319  12      4  1079  1050   9
  3  1291  1299  14     17    44    76  44     14   127   105  22      5  1051   968   9
  4  1344  1356  12     18   384   368  12     15   144   115  21      6  1281  1289  10
  5   359   373   7     19   231   211  14     16   -54    87  34      7   538   591   6
  6   431   208   8     20   369   366  13     17   103   177  24      8   475   491   6
  7  1796  1826  16     21   131   122  22     18   126   110  22      9   233   212   7
  8  -100   197  16     22  -109    13  22     19   -57    65  36     10   593   513   7
  9   140   196  13                            20   -31    11  51     11   320   257   7
 10   -33    38  34      h   7    0                                  12   692   715   8
 11   -53    39  26                             h  12    0           13   445   425   8
 12   481   459  10      7   431   553  13                           14   433   428   8
                         8    90    29  18     12   233   195  21     15   -39    44  30
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Tetrakis(C6F5)-Octachloroporphinato Zinc 6(C6H4Cl2)   Page   2

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16   193   217   11     6   268   230    6    15   247   241   11    12    47    23   24
17   -78    30   20     7   597   526    7    16   434   396   10    13   -79    39   16
18   -79    58   21     8   347   370    7    17    54    56   26    14   332   303    8
19    30    70   36     9   806   746    8    18   318   288    9    15   252   232   10
20   350   358    9    10   676   705    8    19    71    71   24    16   107   142   17
21   -91    22   18    11   -19    16   36    20   260   226   10    17   449   457    9
22   157   170   14    12   529   564    8    21    78    69   24    18   181   201   13
23    40    44   36    13    59   112   23                          19   159   141   12
                       14   479   509    8     h  10    1          20    -9    47   52
     h   2   1         15   148   125   13                          21   -90    57   18
                       16   470   461    9    11   308   372    9    22    97    94   20
 3   384   361    5    17   -49    55   30    12   254   271   10
 4   828   771    7    18   399   403    8    13   334   348    9     h   1    2
 5  1293  1233   10    19   212   204   10    14   206   186   12
 6  1003   904    9    20   432   410    9    15   165   151   14     1  1160  1091   11
 7   545   502    6    21   155   155   14    16    70    81   22     2   493   518    5
 8   470   425    6    22   183   178   13    17   245   231   10     3   951   913    8
 9   604   601    7                           18   150   160   14     4   772   739    7
10   135   144   10     h   6   1            19    -5    78   57     5   720   758    7
11   731   759    8                           20    88   110   21     6   162   152    7
12   578   545    8     7   218   179    7                           7  1957  1983   16
13   595   561    8     8   588   658    7     h  11    1             8   323   304    6
14   476   396    8     9   387   400    7                           9  1034   966    9
15   -33    60   33    10   380   381    7    12   141   137   14    10   462   470    7
16   107   139   17    11   759   792    9    13    65   101   25    11   885   814    9
17   501   506    9    12   189   247   10    14   205   301   12    12   641   603    8
18   141    60   15    13   260   250    9    15   113   171   18    13   550   551    8
19   493   499    8    14   253   256   10    16   194   221   11    14   341   356    8
20   119    90   16    15   279   280   10    17   -63    44   24    15   442   440    9
21   242   240   10    16   -64    18   24    18   217   206   11    16   214   240   11
22   -61    19   26    17   187   213   13    19    62    73   27    17   226   246   11
23   -66    54   34    18   148   210   13    20   193   168   13    18   -66    67   25
                       19   462   464    8                          19   285   286    9
     h   3   1         20   -46    70   31     h  12    1            20    85    85   20
                       21   131   162   16                          21   180   174   12
 4  1038  1041    9    22   -64    83   26    13   370   362   10    22   122   140   17
 5  1346  1350   11                           14   120   160   17
 6   776   811    7     h   7   1            15   359   316    8     h   2    2
 7  1048  1112    9                           16   126   158   15
 8   640   596    7     8   802   763    8    17   239   254   10     2   115   222   11
 9   411   411    7     9   462   468    7    18    95    98   20     3   499   541    5
10   411   379    7    10   642   577    8    19   211   186   12     4   975   972    8
11   107   122   12    11   438   440    8                           5  1246  1329   10
12   525   441    8    12   302   305    8     h  13    1             6   575   578    6
13   220   233    9    13   183   215   11                           7   791   832    8
14   607   630    8    14   306   237    9    14   -53   106   25     8   125   164   10
15   371   375    9    15   152   178   13    15   146   123   13     9   188   151    8
16   138   152   14    16   263   300   10    16   173   182   12    10   334   323    7
17   239   271   11    17   167   192   14    17   126   176   16    11   221   250    8
18   502   513    9    18   193   219   11    18   142   143   15    12   390   350    8
19   -87    49   17    19   -87    39   18    19   140   120   16    13   177   123   10
20   211   228   11    20   240   249   10                          14   494   470    8
21    87    68   21    21   140   105   15     h  14    1            15   212   184   11
22   -51    23   30    22   -76    53   31                          16   263   256   10
                                              15   201   217   11    17   210   231   12
     h   4   1          h   8   1            16   226   251   11    18   161   198   14
                                              17    79    35   23    19   331   333    9
 5   603   551    6     9   -36    98   27    18   107   122   19    20   413   428    9
 6  1198  1138   10    10   234   283    9                           21   138   138   15
 7  1166  1138   10    11   415   462    8     h  15    1            22   174   183   13
 8   824   881    8    12   436   459    8
 9   206   301    8    13   321   323    9    16   401   398    9     h   3    2
10   782   756    8    14   279   273   10    17   171   120   13
11   -22   169   34    15   471   451    9                           3  2365  2372   21
12   192   220    9    16   213   236   12     h   0    2             4  1316  1274   11
13   554   545    8    17    78    82   20                           5  1676  1624   13
14   279   298    9    18   -80    45   19     0  2468  2461   17     6   564   468    6
15   247   272   10    19   222   276   11     1   848   810    7     7   422   366    6
16   183   221   12    20   139   131   15     2    74    32   11     8  1195  1216   10
17   470   464    9    21   129   146   16     3   641   555    6     9   360   355    7
18   154   167   15                            4  1238  1198   10    10   535   476    7
19   156   155   13     h   9   1             5   733   762    7    11   343   378    7
20   162   148   13                            6   337   297    6    12   272   277    8
21   424   385    9    10   598   572    8     7   158   149    8    13   589   602    8
22   103    82   19    11   392   403    8     8   562   501    7    14   409   380    8
                       12   401   387    8     9   316   350    7    15   328   320    9
     h   5   1         13   681   698    9    10   846   868    8    16   185   169   12
                       14   495   527    9    11    99    98   13    17   394   393    9
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Tetrakis(C6F5)-Octachloroporphinato Zinc 6(C6H4Cl2)   Page 3

18	86	110	22
19	386	369	8
20	105	94	18
21	157	170	14
22	-69	36	24

h 4 2

4	1785	1774	16
5	1106	1040	9
6	1360	1250	11
7	883	843	8
8	633	670	7
9	498	480	7
10	230	257	8
11	28	120	31
12	345	360	8
13	166	163	11
14	540	509	8
15	340	371	9
16	330	344	9
17	317	303	10
18	370	389	8
19	219	191	10
20	324	330	9
21	19	40	46
22	92	108	21

h 5 2

5	1236	1130	12
6	481	498	6
7	523	601	7
8	414	463	7
9	422	386	7
10	399	352	7
11	310	303	8
12	346	300	8
13	530	549	8
14	194	149	11
15	41	75	31
16	368	384	9
17	365	380	10
18	101	93	17
19	255	253	10
20	156	112	13
21	356	318	9
22	24	79	44

h 6 2

6	435	459	9
7	314	223	7
8	252	252	7
9	234	248	8
10	878	857	9
11	145	188	11
12	497	494	8
13	116	132	15
14	473	440	9
15	316	242	9
16	242	214	11
17	-55	96	28
18	275	286	9
19	171	187	12
20	183	192	12
21	187	193	12
22	113	137	18

h 7 2

7	942	715	11
8	656	589	8
9	633	607	8
10	145	117	11
11	344	331	8
12	389	410	8
13	473	532	8

14	206	211	11
15	96	96	19
16	233	243	11
17	260	272	10
18	164	126	12
19	268	284	10
20	284	260	10
21	145	128	15

h 8 2

8	757	726	11
9	366	297	8
10	661	702	8
11	346	389	8
12	331	315	9
13	332	374	9
14	325	325	9
15	311	364	10
16	114	137	18
17	92	96	18
18	329	341	9
19	23	77	43
20	267	260	10
21	180	196	13

h 9 2

9	1043	959	13
10	43	85	28
11	452	398	8
12	449	458	9
13	323	336	9
14	184	176	12
15	284	340	10
16	160	210	14
17	386	386	8
18	75	69	22
19	134	180	15
20	100	110	19
21	125	153	19

h 10 2

10	395	328	12
11	346	357	9
12	215	275	11
13	234	243	11
14	414	435	9
15	99	89	20
16	282	255	9
17	116	116	16
18	174	183	12
19	81	74	22
20	262	216	11

h 11 2

11	753	725	12
12	173	188	12
13	523	520	9
14	-51	67	30
15	253	296	9
16	-49	18	28
17	225	222	11
18	178	150	12
19	94	124	20
20	47	33	33

h 12 2

12	64	66	34
13	79	95	23
14	51	147	27
15	171	149	12
16	250	246	10
17	107	97	18
18	155	180	14

19	88	79	22

h 13 2

13	105	201	24
14	122	116	15
15	289	297	9
16	-91	46	18
17	-51	79	29
18	115	107	18

h 14 2

14	338	329	12
15	343	307	9
16	208	205	11
17	114	129	18
18	148	170	15

h 15 2

15	292	324	14
16	73	108	24
17	38	81	37

h 16 2

16	262	262	15

h 0 3

1	2683	2563	21
2	2509	2369	18
3	290	311	6
4	449	476	6
5	25	80	26
6	590	612	7
7	124	98	10
8	-6	14	42
9	1406	1395	12
10	131	155	11
11	409	418	7
12	496	471	8
13	518	554	8
14	52	43	26
15	104	117	17
16	13	65	49
17	151	88	14
18	159	80	12
19	389	313	8
20	423	380	9
21	147	160	14
22	139	120	15

h 1 3

2	2875	2782	20
3	450	415	6
4	208	228	6
5	563	533	6
6	893	970	8
7	475	480	6
8	425	447	7
9	333	323	7
10	422	476	7
11	211	194	9
12	356	381	8
13	431	458	8
14	443	477	8
15	68	156	23
16	432	415	9
17	174	157	13
18	360	335	8
19	186	186	11
20	-45	48	31
21	180	181	12
22	158	173	14

h 2 3

3	440	423	6
4	379	415	6
5	235	246	6
6	168	207	8
7	505	482	7
8	492	563	7
9	611	613	7
10	379	374	8
11	460	437	7
12	179	238	10
13	195	243	10
14	213	179	10
15	396	418	9
16	281	257	10
17	132	162	16
18	122	90	14
19	242	182	10
20	119	138	16
21	-73	28	22
22	96	121	20

h 3 3

4	441	436	6
5	682	714	7
6	376	403	6
7	129	70	10
8	400	492	7
9	367	371	7
10	289	348	8
11	143	108	11
12	691	658	8
13	374	372	8
14	-70	95	20
15	39	68	32
16	633	622	9
17	166	231	14
18	186	177	11
19	183	135	12
20	466	398	9
21	-39	57	34
22	105	133	19

h 4 3

5	772	817	8
6	416	452	6
7	315	275	7
8	511	514	7
9	727	695	8
10	602	613	8
11	496	435	8
12	463	473	8
13	352	363	8
14	178	252	12
15	92	155	19
16	340	323	10
17	280	279	11
18	230	191	10
19	537	518	8
20	184	158	12
21	92	86	20
22	79	82	23

h 5 3

6	269	263	7
7	493	517	7
8	1156	1173	10
9	265	284	8
10	350	378	8
11	269	256	8
12	738	677	9
13	191	164	11
14	210	193	11
15	262	293	10

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16	344	331	10	14	46	138	32	4	190	190	8	15	172	141	13
17	78	95	23	15	447	367	8	5	952	916	9	16	519	528	9
18	206	199	11	16	187	176	11	6	783	696	8	17	72	86	21
19	253	218	10	17	186	188	12	7	392	330	7	18	314	302	9
20	161	168	13	18	-38	65	34	8	83	37	14	19	71	40	23
21	-91	4	18	19	-20	74	46	9	694	630	8	20	372	361	9
22	74	89	45	20	92	127	21	10	199	150	9	21	118	89	17

h   6   3   h   11   3

								11	316	276	8				
7	375	408	7	12	455	395	9	12	704	688	9	h	5	4	
8	352	377	7	13	145	173	15	13	371	347	8				
9	754	792	8	14	73	104	25	14	-69	90	21	5	656	716	10
10	-28	152	32	15	154	181	13	15	205	171	11	6	446	431	7
11	204	146	10	16	196	209	11	16	34	47	37	7	765	808	8
12	285	266	9	17	239	238	10	17	42	48	34	8	361	313	7
13	438	456	8	18	133	153	15	18	-76	20	19	9	319	330	8
14	224	247	10	19	-39	59	35	19	185	201	12	10	233	240	9
15	192	213	12					20	214	229	11	11	225	238	9
16	218	173	12	h	12	3		21	95	89	20	12	246	194	9
17	86	141	19					22	46	70	38	13	103	151	17
18	-40	26	31	13	-72	112	23					14	272	283	10
19	189	184	12	14	172	190	12	h	2	4		15	332	298	10
20	-22	64	43	15	91	47	19					16	171	193	14
21	137	143	15	16	228	197	11	2	741	739	9	17	-73	22	20
				17	159	95	13	3	142	155	9	18	86	101	20
h	7	3		18	-59	3	27	4	283	303	7	19	258	274	10
				19	187	158	13	5	500	479	7	20	92	119	20
8	630	593	8					6	758	718	8	21	-46	40	32
9	438	404	8	h	13	3		7	259	283	7				
10	629	585	8					8	908	881	9	h	6	4	
11	208	240	10	14	197	165	11	9	470	433	7				
12	384	312	8	15	110	91	17	10	256	248	8	6	788	762	11
13	268	224	10	16	205	175	11	11	493	441	8	7	138	203	10
14	307	281	9	17	90	103	21	12	265	286	9	8	689	612	8
15	227	171	11	18	-80	36	21	13	262	227	9	9	473	442	8
16	-46	118	32					14	138	155	14	10	342	320	8
17	185	180	11	h	14	3		15	87	69	20	11	232	191	10
18	353	351	9					16	428	441	9	12	276	220	9
19	148	132	14	15	405	384	9	17	-29	43	41	13	140	167	14
20	193	195	12	16	218	198	11	18	134	84	14	14	299	296	10
21	-82	52	21	17	168	168	14	19	227	187	10	15	276	291	10
								20	105	103	18	16	329	269	10
h	8	3		h	15	3		21	120	119	17	17	32	58	35
												18	102	158	18
9	166	206	10	16	74	102	24	h	3	4		19	116	91	17
10	180	129	10									20	179	166	13
11	820	836	9	h	0	4		3	668	703	9	21	51	45	31
12	100	122	17					4	565	546	7				
13	125	128	15	0	525	515	8	5	937	914	9	h	7	4	
14	225	193	11	1	748	788	7	6	234	272	7				
15	386	380	9	2	1660	1612	13	7	166	132	9	7	786	741	11
16	87	115	22	3	680	754	7	8	266	237	7	8	442	520	8
17	72	91	22	4	639	618	7	9	291	314	8	9	847	819	9
18	-107	13	14	5	257	270	7	10	310	272	8	10	206	219	10
19	270	269	10	6	380	335	6	11	73	98	19	11	531	523	8
20	-28	17	41	7	158	177	9	12	582	592	8	12	256	241	10
21	133	144	16	8	253	279	7	13	326	326	9	13	179	213	12
				9	416	457	7	14	38	112	32	14	264	232	10
h	9	3		10	214	238	9	15	563	540	9	15	137	158	16
				11	392	341	8	16	259	207	11	16	187	200	11
10	395	382	8	12	687	698	9	17	114	97	18	17	211	217	11
11	367	379	9	13	57	153	24	18	78	97	21	18	165	160	13
12	37	94	33	14	464	476	9	19	521	535	9	19	300	289	10
13	110	92	17	15	44	92	31	20	115	132	17	20	23	16	44
14	317	325	10	16	361	359	9	21	173	183	13				
15	281	234	11	17	221	253	12					h	8	4	
16	306	281	9	18	392	381	8	h	4	4					
17	135	149	14	19	117	128	16					8	493	474	11
18	207	219	11	20	198	182	12	4	986	897	11	9	487	492	8
19	-105	39	15	21	-37	27	36	5	380	371	7	10	862	894	10
20	55	96	29	22	287	271	12	6	778	800	8	11	423	457	9
								7	545	561	7	12	324	350	9
h	10	3		h	1	4		8	364	314	7	13	235	184	11
								9	290	286	8	14	291	289	10
11	211	281	11	1	284	259	8	10	60	117	21	15	-60	83	27
12	287	231	10	2	545	483	6	11	143	200	12	16	190	224	11
13	712	607	10	3	225	224	7	12	1167	1160	11	17	165	147	12
								13	454	421	8	18	316	309	9
								14	226	237	10	19	-73	42	22

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 20   63   81   27        5   608  658   7       17   292  282    9        9   479  461    8
                          6   189  204   8       18   363  354    9       10   158  149   12
   h   9   4              7   371  383   7       19   143  125   14       11   492  485    9
                          8   191  162   9       20   271  267   10       12   -47   49   29
  9   526  509   11       9   748  644   8       21   112  129   18       13   256  240   11
 10    76  119   20      10   -48   30  24                                14   253  260   11
 11   141   56   14      11   298  192   9          h   4   5             15   137  129   13
 12   441  411    9      12   522  494   8                                16   205  226   11
 13   362  335    9      13   659  553   9        5   509  486    7       17   213  219   11
 14   381  380   10      14   202  190  11        6   459  478    7       18    39   37   35
 15   178  168   11      15   -60   20  25        7   243  223    8       19   164  146   14
 16   183  155   11      16    40   51  35        8   383  416    8
 17   324  334    9      17   167  170  12        9   270  251    8          h   9   5
 18   150  123   14      18   -57   69  25       10   383  395    8
 19   112  114   18      19   296  299  10       11   479  511    8       10   304  295    9
 20   202  216   12      20   -49    3  30       12   154  149   13       11   390  367    9
                         21   177  199  13       13   127  141   15       12   199  230   12
   h  10   4                                      14   141  136   14       13   -69  123   24
                           h   1   5             15   395  415   10       14   401  410    8
 10   228  245   14                               16   380  322    9       15   193  209   11
 11   299  307    9       2   298  355   7       17   139  170   14       16   294  298    9
 12   192  209   12       3   553  618   7       18   285  278    9       17   108   61   17
 13   -48   59   31       4   274  214   7       19   501  460    9       18    87   95   21
 14   201  209   12       5   681  715   8       20    94   97   20       19    19   62   47
 15    92  133   18       6   854  845   9       21    73   82   34
 16   463  465    8       7   321  383   7                                   h  10   5
 17   115  119   17       8   773  747   8          h   5   5
 18    77  114   23       9   598  640   8                                11   153  137   14
 19   -70   54   24      10   292  271   8        6   524  474    7       12   117  180   17
                         11   252  234   9        7   432  426    7       13   205  222   12
   h  11   4             12   480  481   8        8   461  386    8       14   232  193   10
                         13   161  190  12        9   341  334    8       15   468  447    8
 11   393  401   13      14    19  123  44       10   298  249    9       16   155  156   13
 12   170  201   13      15   -86   38  19       11   282  261    9       17   226  231   11
 13   202  210   12      16   235  234  11       12   202  243   11       18   244  211   11
 14   196  171   11      17   -46   10  28       13   376  371    9
 15   247  278   10      18    90  126  19       14   142  163   15          h  11   5
 16   390  376    9      19   -19   85  45       15   235  264   11
 17   207  181   11      20    62   91  27       16   200  217   10       12   361  399   10
 18   114  133   17      21    97   63  20       17   -71   69   21       13   229  235   10
 19   251  253   11                               18    84  102   21       14   103  143   17
                           h   2   5             19    62   88   26       15   114  132   17
   h  12   4                                      20   149  144   15       16   264  250   10
                          3   596  605   7                                17   125   86   16
 12   409  448   13       4   537  485   7          h   6   5             18   224  211   12
 13   107  148   16       5   928  929   9
 14    59   86   25       6   207  213   8        7   132  151   12          h  12   5
 15   -51   53   28       7   705  671   8        8   484  413    8
 16   104  117   18       8   345  299   7        9   289  304    9       13    52  145   28
 17   -53   43   29       9   606  633   8       10   291  281    9       14   144  180   14
 18   -63   31   26      10   210  201   9       11   380  364    9       15   -79   95   20
                         11   354  356   8       12   282  296   10       16   160  127   14
   h  13   4             12   231  224  10       13   177  188   12       17    99  129   20
                         13   469  462   9       14   166  216   13
 13   134  158   20      14   232  228  11       15   289  257   10          h  13   5
 14   -72   55   21      15   418  375   9       16    96  147   18
 15   198  216   12      16    37   75  37       17   197  231   11       14   241  271   10
 16    70   99   25      17   181  143  11       18   210  224   11       15   102  103   19
 17   182  206   13      18   187  183  12       19   208  214   12       16   191  201   12
                         19   180  213  12       20    69   35   25       17    37   39   48
   h  14   4             20   157  116  14
                         21   117  119  18          h   7   5                h  14   5
 14   523  478   12
 15    92   79   20        h   3   5              8    85   87   17       15   150  162   14
 16   201  187   12                               9   128  100   13       16   183  186   13
 17   109   86   26       4   396  387   7       10   472  448    8
                          5   456  480   7       11   393  348    9          h   0   6
   h  15   4              6   467  481   7       12   450  455    9
                          7   271  274   8       13   112  100   17        0  1466 1440   10
 15   -97   50   24       8   432  412   7       14   432  426    9        1   691  627    8
 16   205  194   12       9   315  286   8       15   -42   77   29        2  1081 1032   10
                         10   337  373   8       16   103  130   17        3   365  390    7
   h   0   5             11   435  426   8       17   108  114   17        4    77   46   16
                         12   703  667   9       18   355  342    9        5   151   58   10
  1   316  294    6      13    97   73  18       19   106   63   18        6    46   42   24
  2   381  327    6      14   205  175  11       20   243  219   11        7    92  159   15
  3   512  502    7      15   186  118  12                                 8   282  355    8
  4   184  233    8      16   449  442  10          h   8   5
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 9   121  141  14          h   4   6          12  376  349  10        16  -59   71  25
10   238  284  10                              13  192  164  13        17  -66   60  23
11   284  329   9           4  361  351  10    14  268  234   9        18   31   17  39
12   229  300  10           5  108   44  13    15  -18   18  45        19  140  167  15
13   104   86  17           6  333  349   8    16  235  250  10
14   114   58  17           7  132   72  12    17  -16   33  48          h   1   7
15   195  213  13           8  600  587   8    18   63   70  27
16   119  156  15           9  168  170  11                             2  160  193  10
17   185  201  12          10  195  147  11      h   9   6              3  424  378   8
18   -89   51  18          11  174  127  12                             4  550  584   8
19   -28   30  40          12  351  297   9     9  685  711  12         5  216  237   9
20   233  189  11          13  219  220  11    10   50   46  30         6  384  396   8
                           14  332  294  10    11  171  123  13         7  340  328   8
   h   1   6               15  272  317   9    12  305  285  10         8  360  374   8
                           16  202  193  11    13  233  216  10         9  275  290   9
 1  1454 1444  10          17  265  310  10    14  237  188  10        10  157  194  13
 2   446  446   7          18  237  198  11    15  256  232  10        11   67  125  23
 3   349  351   7          19   94   40  20    16  125  142  16        12  246  318  11
 4   605  554   8          20  109  142  19    17  404  381   9        13  282  264  10
 5   341  321   7                              18   80   77  23        14  196  202  10
 6   271  261   8            h   5   6                                 15   59   69  25
 7   526  479   8                               h   10   6             16  112  116  17
 8   335  289   8           5  862  894  12                            17   74   69  23
 9   561  563   8           6  150  181  11    10   97   88  27        18   81   71  22
10    94  110  17           7  237  256   9    11  154  125  14        19  132  118  16
11   391  386   9           8   86  182  18    12  189  179  11
12   -24   59  40           9  294  320   9    13  253  230  10          h   2   7
13   148  168  14          10  148  145  13    14  183  157  12
14    86   23  21          11  238  267  10    15   97  122  19         3  648  643   8
15   378  345  10          12  191  192  12    16  146  130  14         4  238  230   9
16   121  142  15          13  360  349   9    17   19   61  47         5  147  205  12
17   -90  105  17          14   71   34  25                            6   52   56  25
18    72   68  23          15  230  235  10      h   11   6            7  224  200  10
19   232  188  11          16  -55    8  26                            8  156  206  12
20    35   83  38          17  106   97  17    11  486  443  11        9  218  240  10
                           18  103  103  18    12  172  181  12       10  -80   17  18
   h   2   6               19  142  152  15    13  134  137  14       11  567  522   9
                                               14  138  152  14       12  171  170  13
 2  1337 1262  14            h   6   6          15  294  264  10       13  379  403  10
 3   321  329   7                              16   95  113  20       14  189  191  11
 4   107  107  12           6  268  341  12    17  163  158  14       15  117   94  15
 5   422  418   7           7  325  350   8                           16  214  181  11
 6   264  242   8           8  188  217  11      h   12   6           17  181  149  12
 7   342  317   8           9  299  292   9                           18  163  153  13
 8   805  827   9          10  525  505   9    12  253  231  14       19  153  160  15
 9   477  506   8          11  342  350   9    13  189  194  12
10   122  140  14          12  314  307  10    14  177  125  12         h   3   7
11   213  221  10          13   63   59  26    15  224  231  11
12   539  537   9          14  305  303  10    16  132  119  16        4  280  257   8
13   112  118  17          15  297  283   9                           5  246  245   9
14   -73   66  22          16  269  289  10      h   13   6           6  419  390   8
15    42   40  35          17  -40   32  33                           7  255  213   9
16    81   67  20          18  159  158  14    13  383  327  13       8  233  240  10
17   -57   36  26          19  257  232  11    14  127  135  16       9  110   87  16
18   315  280   9                              15   69  100  25      10  163  145  13
19   293  303  10            h   7   6                               11  155  153  13
20   184  183  13                                h   14   6          12  255  274  11
                            7  332  296  12                          13   33   79  38
   h   3   6                8  132   84  14    14  114  138  24      14  397  365   8
                            9  390  368   9    15   80  101  32      15  157  162  13
 3   419  458  10          10   90   49  19                          16  -38   96  33
 4   450  441   7          11  316  280   9      h   0   7           17  369  339   9
 5   452  460   7          12  170  145  13                          18  366  359   9
 6    70   36  18          13  378  390  10     1  424  385   7      19  192  186  13
 7   293  336   8          14  195  158  11     2  300  310   8
 8   199  179  10          15  126  168  15     3  118  139  13        h   4   7
 9   379  375   8          16   49   95  30     4  146  192  11
10   267  232   9          17  -49   59  29     5  152  162  11       5  352  303   8
11   319  325   9          18  134  114  15     6   67   28  20       6  212  218  10
12   281  292  10          19  226  200  11     7  923  911  10       7  469  521   8
13   454  430   9                              8  416  338   8       8  235  204  10
14    83  102  22            h   8   6          9  175  146  12       9  237  250  10
15   191  212  13                              10  188  188  11      10   82  100  20
16   148  228  13           8  323  393  13    11  172  121  12      11  239  239  11
17   294  270   9           9  -52   47  26    12  -55   18  27      12   88  130  21
18   211  175  11          10  257  291  10    13   48   86  32      13  111   56  18
19   259  201  10          11   95  138  19    14  -35   51  33      14   64   35  23
20   129  107  16                              15  202  195  11      15  226  206  10
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16  230  208  11        14   86   51  21        13  134  153  14         9  277  233  11
17  274  264  10        15  176  148  13        14  206  195  11        10  134  137  13
18  103   83  19        16   54   26  30        15  173  132  12        11  375  382   8
19   91   85  24                                16   66   67  25        12  162  187  12
                        h  11   7               17   78   90  23        13   21   36  44
 h   5   7                                      18  282  294  10        14  133  155  15
                        12   98  109  18                                15  147  164  14
 6  317  286   9        13  124   91  16         h   3   8               16   67   88  26
 7  320  306   9        14  231  237  11
 8  262  209  10        15   33   85  38         3  118  188  20         h   8   8
 9  162  191  13        16   47   97  33         4  124  136  14
10  432  425   9                                 5  139  155  13         8  428  418  13
11  234  198  11        h  12   7                6  241  256  10         9   93   78  21
12  185  118  13                                 7  534  531   9        10   74  137  21
13  162  133  14        13  218  250  11         8  214  205  11        11  138  162  14
14  166  145  12        14  165  153  13         9  263  261  10        12  194  204  11
15  108   74  17        15  207  187  12        10  102   96  19        13  244  254  10
16  215  188  11                                11  195  203  13        14  215  209  11
17  167  136  13        h  13   7               12  139  138  13        15  158  108  14
18  180  172  13                                13  252  284  10        16  197  209  12
                        14  168  176  14        14  -56   34  26
 h   6   7                                      15   28   78  40         h   9   8
                        h   0   8               16  198  182  12
 7  350  365   9                                17  263  277  10         9  312  316  12
 8  104  113  17         0  276  380  12        18   38   35  48        10  -76   43  19
 9   99  110  18         1  -38   13  29                               11  243  225  10
10  240  281  11         2  104   17  16         h   4   8              12  126  122  15
11  508  557   9         3  -60   55  22                               13  167  170  13
12  216  217  12         4  122  106  14         4  113   99  22        14   46   35  32
13  248  249   9         5  183  206  11         5  194  237  11        15  137  113  16
14  126  129  15         6  394  400   9         6  320  287   9
15   61  114  26         7  -39    2  31         7   83   72  20         h  10   8
16  -74   32  21         8  615  623   9         8  230  239  11
17   55   85  29         9   69    7  23         9  -89   66  18        10  233  258  14
18  118  149  17        10   69   96  24        10  292  273  10        11   73   98  23
                        11  -77   18  21        11  117   86  18        12   63   96  26
 h   7   7             12  156  126  15        12  231  225  10        13  -31  101  38
                        13  -35   32  33        13  138  141  14        14   20   92  46
 8  448  433   9        14  110  146  16        14  275  291  10        15  109  132  19
 9   99  100  18        15   11   79  51        15  176  146  12
10   57  132  28        16  -41   13  33        16  101  106  19         h  11   8
11  125  108  17        17   84   38  22        17  201  216  12
12  532  490  10        18  133   78  16                               11  184  204  17
13   31   73  36                                 h   5   8              12   47   31  31
14  -87   62  18        h   1   8                                      13  250  226  11
15   70  117  24                                 5  213  229  15        14   89   81  21
16  184  198  12         1  149  169  17         6  137  132  14
17  128  148  16         2   78   69  19         7  177  160  12         h  12   8
18   28   76  42         3  238  278  10         8  259  279  10
                        4  214  208  10         9  200  219  12        12  143  180  21
 h   8   7              5  170  169  12        10  119  140  17        13   78   59  23
                        6  201  205  11        11  234  227  11
 9  661  664   9         7  438  427   9        12  164  143  12         h   0   9
10  135  138  16         8  240  253  10        13  209  226  11
11  277  251  11         9  377  328   9        14   96   73  19         1  762  726   9
12  270  245   9        10  282  274  10        15  102   76  18         2  187  126  12
13  137  153  14        11  315  277  10        16  162  127  13         3  677  646   9
14  -45   53  30        12  255  267  11        17  245  240  11         4  138   76  14
15  167  187  13        13  148  103  13                                5  229  229  11
16   57   49  28        14  177  169  12         h   6   8               6   92   76  19
17  159  144  14        15  139  118  14                                7  564  604   9
                        16  121  107  16         6  196  208  16         8  236  239  11
 h   9   7             17  113   94  18         7   63   65  25         9  -48   20  31
                        18  -37   35  37         8   50   80  30        10  152   91  12
10  189  196  13                                 9   56    5  29        11  230  208  10
11  183  203  11        h   2   8               10  246  214  11        12  167  164  12
12  231  253  10                                11   64   71  23        13   48   99  30
13  253  244  10         2  256  220  13        12  381  373   8        14  165  189  13
14  148  116  14         3  362  368   8        13   27   27  39        15   83   77  22
15  181  162  12         4  324  313   9        14   83   85  21        16  112  100  18
16  283  291  10         5  155  213  12        15   30   48  39
17   50   84  31         6  250  272  10        16  161  160  14         h   1   9
                        7  514  465   9        17  115  112  18
 h  10   7              8   86   64  20                                 2  451  463   9
                        9  171  153  13         h   7   8               3  193  224  11
11  381  372   8        10  306  310  10                                4  257  190  10
12  -67   62  22        11  155  142  14         7  334  276  13         5  258  289  10
13  235  230  10        12  433  400   9         8  -24   60  43         6  275  299  10
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Tetrakis(C6F5)-Octachloroporphinato Zinc 6(C6H4Cl2)   Page   8

7	108	36	18	11	374	362	9									
8	290	289	10	12	276	234	10	h	2	10			h	8	10	
9	45	60	33	13	137	171	15									
10	249	242	9	14	48	34	31	2	171	206	19		8	195	248	16
11	44	67	30	15	59	96	28	3	83	124	22		9	125	126	16
12	105	144	17					4	120	154	17		10	261	249	10
13	138	132	14	h	7	9		5	169	99	14		11	75	54	24
14	157	155	13					6	228	258	10		12	72	77	25
15	96	94	20	8	152	193	13	7	165	145	12					
16	93	47	21	9	155	149	13	8	145	156	13		h	9	10	
				10	279	304	9	9	157	166	13					
h	2	9		11	122	96	16	10	191	174	12		9	86	95	29
				12	27	38	41	11	43	16	32		10	71	45	25
3	193	171	11	13	232	220	11	12	-79	79	21		11	77	106	24
4	208	173	11	14	164	145	14	13	-41	47	33					
5	147	151	14	15	54	91	30	14	135	134	16		h	10	10	
6	97	73	19													
7	360	371	10	h	8	9		h	3	10			10	124	107	23
8	96	137	20													
9	209	175	12	9	232	249	10	3	310	302	14		h	0	11	
10	184	145	11	10	173	119	12	4	118	98	18					
11	316	297	9	11	129	113	15	5	206	198	10		1	29	13	37
12	6	45	55	12	168	154	13	6	92	99	18		2	-52	67	27
13	91	176	20	13	163	142	14	7	181	182	11		3	239	234	10
14	81	62	22	14	156	153	14	8	199	177	11		4	250	262	10
15	100	60	19					9	153	149	13		5	172	149	12
16	67	52	26	h	9	9		10	103	149	18		6	-76	26	21
								11	174	191	13		7	95	133	19
h	3	9		10	-75	49	21	12	78	53	23		8	76	95	23
				11	94	87	20	13	197	164	12		9	100	60	19
4	344	318	9	12	120	129	17	14	62	53	28		10	50	82	31
5	150	149	14	13	88	75	21						11	186	158	13
6	334	310	10	14	136	133	22	h	4	10			12	90	34	21
7	62	78	26													
8	125	121	17	h	10	9		4	121	123	22		h	1	11	
9	201	147	13					5	-48	27	27					
10	368	371	8	11	49	51	31	6	-63	84	22		2	197	202	11
11	122	94	15	12	91	42	21	7	28	44	38		3	135	70	14
12	80	98	21	13	174	142	13	8	109	110	17		4	194	193	11
13	-57	41	26					9	16	7	47		5	209	199	11
14	144	135	14	h	11	9		10	173	164	12		6	270	258	10
15	126	166	16					11	82	113	22		7	146	154	14
16	102	105	20	12	150	112	15	12	202	198	12		8	103	124	18
								13	84	87	22		9	115	107	17
h	4	9		h	0	10		14	125	129	17		10	201	189	12
													11	75	93	24
5	119	125	16	0	-21	39	57	h	5	10			12	73	53	25
6	167	192	13	1	-32	13	38									
7	289	348	10	2	467	423	9	5	144	191	18		h	2	11	
8	147	135	15	3	102	45	19	6	42	30	31					
9	168	189	12	4	221	215	12	7	144	130	13		3	103	66	17
10	199	143	11	5	307	298	10	8	-54	39	27		4	68	82	23
11	87	91	20	6	125	81	14	9	102	84	18		5	57	56	27
12	127	186	15	7	187	172	11	10	-28	45	40		6	95	39	19
13	176	155	12	8	144	160	13	11	133	134	15		7	233	235	11
14	68	98	25	9	95	125	18	12	94	56	20		8	129	163	15
15	-43	69	33	10	233	191	10	13	202	186	12		9	134	122	15
16	175	135	13	11	197	181	12						10	108	88	18
				12	79	102	22	h	6	10			11	76	69	24
h	5	9		13	79	10	23						12	-50	57	35
				14	-19	60	47	6	132	144	20					
6	202	196	12					7	156	168	13		h	3	11	
7	42	63	34	h	1	10		8	152	133	13					
8	219	187	12					9	93	112	19		4	204	220	11
9	49	103	28	1	215	208	17	10	260	259	10		5	111	69	17
10	309	263	9	2	40	18	35	11	138	150	15		6	26	94	41
11	76	48	22	3	186	190	13	12	92	29	21		7	123	94	16
12	79	77	22	4	260	251	11	13	80	60	23		8	170	164	13
13	65	22	25	5	192	155	13						9	172	198	13
14	199	212	12	6	72	50	21	h	7	10			10	163	147	14
15	83	82	22	7	374	372	8						11	56	19	29
				8	134	91	14	7	283	268	13					
h	6	9		9	-78	77	19	8	-27	28	40		h	4	11	
				10	-66	68	23	9	170	213	13					
7	312	356	10	11	178	186	12	10	112	73	17		5	131	95	15
8	159	168	12	12	96	88	19	11	226	203	11		6	70	30	24
9	37	48	33	13	220	189	11	12	176	115	13		7	105	74	18
10	132	169	14	14	55	38	29	13	117	75	25		8	43	62	33

Tetrakis(C6F5)-Octachloroporphinato Zinc 6(C6H4Cl2)   Page   9

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 9   159  149  14      8   148  132  15      1   287  299  14      4   -23   46  44
10   -73   50  23      9   102  103  19      2    69    9  24      5   -37   46  36
11   205  199  12     10   192  205  18      3   179  150  13      6   127  139  16
                                             4   100  103  19      7   136  131  16
 h   5   11            h   8   11            5   122  138  16      8   103  104  19
                                             6    88   30  21
 6   -45   39  31      9   159  194  14      7    95  109  20      h   4   12
 7   120  125  16                            8    93   29  21
 8    90  125  20      h   0   12                                 4   207  179  16
 9   123   96  16                            h   2   12           5    57   29  28
10   126   97  16      0    77  145  31                           6    85   95  22
11    86   53  22      1    30   37  39      2   245  234  15      7   113  120  18
                       2   330  332   9      3    88   57  21
 h   6   11            3    68    5  25      4    82   82  22      h   5   12
                       4    84   25  22      5   126  126  16
 7   205  203  12      5   244  264  11      6   109  105  18      5   -42   51  44
 8    69   27  25      6   269  233  10      7   115   71  18      6    56  106  29
 9   167  130  13      7   156  125  14      8   126  128  17      7    91   74  21
10    81   31  23      8    75   33  24
                                             h   3   12           h   6   12
 h   7   11            h   1   12
                                             3   197  174  17      6   131  137  23
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Table 1. Final Refined Parameters for

Aquo, Carbonyl Tetrakis(Pentafluorophenyl)octachloroporphyrin Ruthenium(II).

$$x, y, z \text{ and } U_{eq}{}^a \times 10^4$$

Atom	x	y	z	U_{eq} or B
Ru	2126(.5)	1763(.5)	1683(.3)	291(2)
Cl1	2662(2)	3927(2)	−61(1)	647(9)
C1	2188(6)	3188(6)	328(3)	2.8(2) *
C2	2635(6)	2714(6)	722(3)	2.3(2) *
N1	1953(5)	2315(4)	990(3)	2.1(1) *
C3	3597(6)	2573(6)	795(3)	2.5(2) *
C4	3997(6)	2090(5)	1169(3)	2.3(2) *
N2	3546(5)	1785(5)	1581(3)	2.1(1) *
C5	4960(6)	1836(6)	1202(4)	3.1(2) *
Cl2	5843(2)	1956(2)	773(1)	748(11)
C6	5069(7)	1380(6)	1619(4)	3.4(2) *
Cl3	6082(2)	876(3)	1761(1)	992(14)
C7	4191(6)	1364(6)	1874(4)	2.8(2) *
C8	4026(6)	1052(6)	2355(4)	2.8(2) *
C9	3163(6)	1023(6)	2593(4)	2.7(2) *
N3	2306(5)	1189(5)	2367(3)	2.4(2) *
C10	2978(7)	796(6)	3109(4)	3.2(2) *
Cl4	3744(2)	581(2)	3587(1)	695(10)
C11	2051(7)	828(6)	3186(4)	3.1(2) *
Cl5	1570(2)	663(3)	3763(1)	813(12)

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Table 1. (Cont.)

Atom	x	y	z	U_{eq} or B	
C12	1613(6)	1046(6)	2710(4)	2.8(2)	*
C13	659(6)	1038(6)	2602(3)	2.5(2)	*
C14	261(6)	1224(6)	2135(3)	2.5(2)	*
N4	715(5)	1586(4)	1736(3)	2.1(1)	*
C15	−708(7)	1098(6)	1993(4)	3.3(2)	*
Cl6	−1575(2)	602(2)	2313(1)	767(11)	
C16	−798(7)	1367(6)	1519(4)	3.4(2)	*
Cl7	−1825(2)	1228(3)	1192(1)	805(11)	
C17	82(6)	1708(6)	1360(3)	2.5(2)	*
C18	263(6)	2147(6)	908(3)	2.5(2)	*
C19	1108(6)	2475(6)	757(3)	2.3(2)	*
C20	1280(6)	3034(6)	342(4)	2.8(2)	*
Cl8	500(2)	3514(2)	−50(1)	718(10)	
C21	4245(6)	2982(6)	425(4)	309(24)	
C22	4358(7)	2698(7)	−51(4)	460(30)	
C23	4973(8)	3078(8)	−388(4)	532(39)	
C24	5459(7)	3762(8)	−242(5)	494(34)	
C25	5369(7)	4056(7)	223(4)	418(31)	
C26	4771(6)	3684(6)	558(4)	347(26)	
C31	4834(6)	696(7)	2634(4)	390(29)	

Table 1. (Cont.)

Atom	x	y	z	U_{eq} or B
C32	4985(7)	−153(7)	2647(4)	460(30)
C33	5726(7)	−491(8)	2911(4)	521(32)
C34	6323(7)	34(9)	3166(4)	564(41)
C35	6179(7)	870(8)	3155(4)	497(34)
C36	5457(7)	1178(7)	2890(4)	485(33)
C41	14(6)	853(7)	3025(4)	375(30)
C42	−182(7)	60(9)	3185(4)	548(36)
C43	−756(8)	−63(10)	3598(5)	655(40)
C44	−1151(9)	600(13)	3840(5)	801(57)
C45	−984(9)	1377(11)	3683(5)	758(46)
C46	−419(7)	1509(8)	3273(4)	544(34)
C51	−564(6)	2279(7)	567(4)	403(29)
C52	−1167(7)	2958(7)	633(4)	472(32)
C53	−1943(7)	3056(8)	342(5)	581(38)
C54	−2128(7)	2515(10)	−26(5)	613(48)
C55	−1549(8)	1857(9)	−110(4)	626(38)
C56	−765(7)	1723(8)	184(4)	487(30)
F22	3874(5)	2015(4)	−195(2)	706(20)
F23	5056(5)	2762(5)	−849(3)	832(25)
F24	6020(5)	4122(5)	−576(3)	818(22)

Table 1. (Cont.)

Atom	x	y	z	U_{eq} or B
F25	5857(4)	4728(4)	369(3)	648(19)
F26	4692(4)	4006(4)	1018(2)	581(18)
F32	4412(4)	−675(4)	2400(3)	665(19)
F33	5841(5)	−1327(4)	2922(3)	768(21)
F34	7021(4)	−306(5)	3428(3)	789(23)
F35	6777(4)	1349(4)	3402(3)	763(22)
F36	5338(4)	2009(4)	2890(3)	741(22)
F42	198(5)	−592(4)	2962(3)	776(23)
F43	−939(5)	−852(6)	3747(3)	1120(29)
F44	−1711(5)	483(7)	4237(3)	1269(38)
F45	−1382(6)	2026(7)	3920(3)	1343(35)
F46	−259(5)	2311(5)	3120(3)	886(24)
F52	−994(4)	3506(4)	1002(3)	714(21)
F53	−2506(5)	3710(5)	414(3)	969(27)
F54	−2872(4)	2604(5)	−321(3)	936(29)
F55	−1730(5)	1297(5)	−476(3)	996(26)
F56	−218(5)	1070(4)	112(3)	801(22)
C61	2044(7)	2772(7)	1999(4)	380(27)
O61	1983(6)	3394(5)	2200(3)	727(27)
O1	2165(4)	550(4)	1319(3)	455(18)

Table 1. (Cont.)

Atom	x	y	z	U_{eq} or B
C71	6734(14)	1512(12)	8525(6)	1339(72)
C72	7369(10)	1351(10)	8083(6)	810(47)
O2	7836(7)	727(6)	8029(4)	1052(36)
O3	7307(8)	1937(6)	7730(5)	1123(39)
C73	7799(23)	1823(15)	7264(11)	2118(126)
C74	7208(30)	1689(27)	6858(12)	3385(205)

^{a} $U_{eq} = \frac{1}{3} \sum_i \sum_j [U_{ij}(a_i^* a_j^*)(\vec{a}_i \cdot \vec{a}_j)]$

* Isotropic displacement parameter, B

Table 2. Assigned Parameters for
Aquo, Carbonyl Tetrakis(Pentafluorophenyl)octachloroporphyrin Ruthenium(II).

x, y, z and $U_{eq}{}^a \times 10^4$

Atom	x	y	z	B	
C81	2113	608	117	10.0	*
C82	3110	277	177	10.0	*
O4	3395	244	596	10.0	*
O5	3902	140	−172	10.0	*
C83	4801	−74	1	13.5	*
C84	5482	37	−378	15.0	*
C91A	4182	1901	8228	15.0	*
C92A	3256	1464	8232	10.0	*
C93A	2614	1851	8622	10.0	*
C94A	1677	1396	8619	10.0	*
C95A	1024	1765	9002	10.0	*
C96A	98	1328	9006	15.0	*
C91B	4073	2287	8474	15.0	*
C92B	3311	1674	8335	10.0	*
C93B	2440	1827	8656	10.0	*
C94B	1666	1226	8527	10.0	*
C95B	806	1382	8845	10.0	*
C96B	44	784	8715	15.0	*
C91C	3801	2164	8479	15.0	*
C92C	3028	1549	8341	10.0	*
C93C	2156	1671	8645	10.0	*
C94C	1405	1091	8521	10.0	*
C95C	545	1247	8840	10.0	*
C96C	−240	644	8712	15.0	*
H71A	6799	1075	8765	10.0	*
H71B	6886	2030	8677	10.0	*
H71C	6100	1528	8413	10.0	*
H73A	8214	1373	7293	10.0	*
H73B	8120	2321	7183	10.0	*
H74A	7585	1586	6569	10.0	*
H74B	6889	1151	6928	10.0	*

Table 2. (Cont.)

Atom	x	y	z	B	
H74C	6796	2099	6818	10.0	*
H81A	1811	602	432	10.0	*
H81B	2131	1164	−8	10.0	*
H81C	1780	265	−113	10.0	*
H83A	4956	271	279	10.0	*
H83B	4801	−643	103	10.0	*
H84A	6077	−112	−249	10.0	*
H84B	5335	−308	−657	10.0	*
H84C	5489	605	−480	10.0	*
H91A	4572	1652	7983	10.0	*
H91B	4093	2474	8150	10.0	*
H91C	4467	1853	8549	10.0	*
H91D	4606	2185	8274	10.0	*
H91E	3859	2841	8419	10.0	*
H91F	4233	2219	8818	10.0	*
H91G	4331	2059	8277	10.0	*
H91H	3589	2719	8423	10.0	*
H91I	3963	2098	8822	10.0	*
H92A	3349	891	8309	10.0	*
H92B	2975	1512	7910	10.0	*
H92D	3528	1121	8391	10.0	*
H92E	3154	1742	7991	10.0	*
H92G	3250	998	8396	10.0	*
H92H	2877	1619	7997	10.0	*
H93A	2518	2424	8546	10.0	*
H93B	2892	1803	8945	10.0	*
H93D	2227	2381	8600	10.0	*
H93E	2600	1759	8999	10.0	*
H93G	1937	2224	8590	10.0	*
H93H	2311	1603	8989	10.0	*
H94A	1777	823	8695	10.0	*

Table 2. (Cont.)

Atom	x	y	z	B	
H94B	1403	1444	8295	10.0	*
H94D	1878	672	8582	10.0	*
H94E	1505	1293	8183	10.0	*
H94G	1616	537	8577	10.0	*
H94H	1243	1158	8178	10.0	*
H95A	927	2338	8926	10.0	*
H95B	1301	1717	9325	10.0	*
H95D	593	1936	8790	10.0	*
H95E	967	1314	9189	10.0	*
H95G	334	1801	8784	10.0	*
H95H	708	1180	9183	10.0	*
H96A	−292	1577	9251	10.0	*
H96B	−187	1376	8685	10.0	*
H96C	187	755	9084	10.0	*
H96D	−483	893	8918	10.0	*
H96E	−122	850	8372	10.0	*
H96F	252	228	8771	10.0	*
H96G	−762	759	8918	10.0	*
H96H	−410	708	8370	10.0	*
H96I	−36	87	8769	10.0	*

Population Parameters: C91A to C96A, 0.302; C91B to C96B, 0.298; C91C to C96C, 0.236. Hydrogen atoms have same population as attached carbon atom; hydrogen atoms A, B and C are on 'A' carbon atoms, D, E and F on 'B' carbon atoms and G, H and I on 'C' carbon atoms. C81, C82, C83, C84 O4 and O5 have population parameter 0.5.

Table 3. Anisotropic Displacement Parameters for
Aquo, Carbonyl Tetrakis(Pentafluorophenyl)octachloroporphyrin Ruthenium(II).

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ru	172(4)	413(5)	289(4)	−13(4)	−3(3)	76(4)
Cl1	392(16)	884(24)	664(21)	−5(16)	37(15)	444(18)
Cl2	327(16)	1175(30)	744(22)	194(17)	208(15)	461(21)
Cl3	358(18)	1677(40)	944(28)	362(21)	171(18)	729(28)
Cl4	400(17)	1312(30)	373(17)	47(18)	−99(13)	225(18)
Cl5	468(19)	1627(37)	343(17)	−69(21)	11(14)	200(20)
Cl6	333(16)	1384(32)	585(21)	−289(18)	−35(14)	397(21)
Cl7	341(16)	1413(34)	659(22)	−267(19)	−130(15)	389(22)
Cl8	350(16)	1152(29)	650(21)	17(17)	−67(14)	526(20)
C21	266(53)	354(63)	308(59)	38(45)	−4(44)	123(47)
C22	519(70)	408(71)	453(75)	−24(57)	−35(59)	−16(58)
C23	464(70)	910(105)	223(62)	222(70)	90(52)	87(65)
C24	286(62)	606(86)	590(86)	28(59)	60(59)	193(70)
C25	226(56)	415(70)	613(83)	−21(51)	−39(54)	117(61)
C26	244(54)	421(66)	374(65)	27(49)	−64(47)	36(53)
C31	261(58)	562(76)	347(64)	−15(54)	17(47)	126(56)
C32	314(60)	643(85)	421(68)	−79(60)	−48(51)	73(61)
C33	414(71)	536(82)	612(81)	238(62)	51(61)	180(65)
C34	243(62)	976(112)	473(76)	62(69)	−74(54)	155(74)
C35	263(62)	645(87)	581(79)	−54(61)	−104(56)	75(67)
C36	290(62)	505(79)	660(82)	−35(58)	−21(58)	134(65)
C41	230(53)	626(79)	268(60)	−47(53)	−1(45)	91(56)
C42	323(66)	863(103)	458(75)	−84(67)	−36(55)	299(73)
C43	458(77)	947(115)	560(91)	−146(77)	−133(67)	361(85)
C44	494(87)	1562(174)	348(83)	−291(103)	55(66)	90(93)
C45	473(82)	1218(137)	583(94)	11(87)	136(70)	−257(95)
C46	355(65)	759(98)	517(78)	−95(63)	49(57)	90(70)
C51	231(54)	608(77)	371(65)	21(53)	6(47)	209(58)
C52	312(63)	629(85)	477(74)	−37(57)	62(55)	100(62)
C53	339(69)	747(102)	656(89)	148(66)	−20(63)	183(75)
C54	186(60)	1063(115)	590(88)	76(71)	−90(60)	235(82)
C55	540(79)	955(106)	380(71)	−247(82)	−187(60)	63(74)
C56	410(65)	628(80)	423(69)	−6(64)	−71(53)	100(66)

Table 3. (Cont.)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
F22	679(45)	876(56)	565(44)	−213(40)	65(35)	−180(39)
F23	767(50)	1276(67)	454(45)	40(46)	170(37)	−103(43)
F24	640(46)	968(57)	849(55)	−34(41)	372(41)	453(45)
F25	495(39)	514(43)	934(54)	−152(34)	45(36)	178(38)
F26	571(41)	698(46)	474(42)	−144(34)	35(32)	−85(35)
F32	564(43)	638(47)	790(51)	8(36)	−206(38)	0(39)
F33	645(47)	747(53)	910(56)	247(40)	−110(40)	54(43)
F34	435(40)	1121(61)	809(52)	162(39)	−250(37)	254(45)
F35	466(41)	945(56)	874(55)	−133(38)	−276(38)	−16(44)
F36	493(42)	722(53)	1007(59)	−118(36)	−222(39)	97(43)
F42	705(51)	603(49)	1021(62)	54(41)	119(44)	131(44)
F43	807(58)	1426(79)	1125(70)	−334(54)	−101(49)	810(63)
F44	741(55)	2569(118)	500(50)	−408(65)	317(43)	118(61)
F45	1057(70)	1987(108)	989(70)	72(69)	472(57)	−628(71)
F46	876(57)	758(57)	1028(63)	22(46)	263(48)	−212(49)
F52	466(40)	839(54)	835(53)	186(36)	−48(37)	−165(43)
F53	533(46)	1258(69)	1115(67)	474(48)	−72(44)	168(54)
F54	385(40)	1701(81)	718(52)	63(46)	−247(37)	208(52)
F55	813(56)	1311(73)	859(60)	−68(50)	−386(47)	−240(54)
F56	776(51)	780(53)	844(56)	201(44)	−269(42)	−226(43)
C61	310(59)	389(69)	442(70)	27(53)	3(50)	66(56)
O61	807(64)	587(63)	787(66)	50(49)	51(50)	−143(51)
O1	438(43)	417(44)	511(47)	−6(35)	−44(35)	3(36)
C71	1856(192)	1558(179)	601(107)	552(146)	−273(118)	−139(112)
C72	777(107)	679(106)	974(127)	5(86)	−104(92)	35(100)
O2	1119(87)	724(72)	1314(95)	293(65)	222(72)	231(67)
O3	1238(94)	876(85)	1255(100)	194(68)	−35(78)	386(75)
C73	3124(411)	1029(170)	2221(315)	292(215)	2029(317)	446(201)
C74	4265(600)	4101(521)	1808(322)	−2050(429)	1958(371)	−1157(350)

$U_{i,j}$ values have been multiplied by 10^4

The form of the displacement factor is:

$$\exp -2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}\ell^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}h\ell a^*c^* + 2U_{23}k\ell b^*c^*)$$

Table 4. Complete Distances and Angles for
Aquo, Carbonyl Tetrakis(Pentafluorophenyl)octachloroporphyrin Ruthenium(II).

	Distance(Å)		Distance(Å)
Ru –N1	2.063(7)	C15 –Cl6	1.711(10)
Ru –N2	2.060(7)	C15 –C16	1.340(14)
Ru –N3	2.059(7)	C16 –Cl7	1.724(11)
Ru –N4	2.052(7)	C16 –C17	1.443(13)
Ru –C61	1.828(10)	C17 –C18	1.420(13)
Ru –O1	2.172(7)	C18 –C19	1.384(12)
Cl1 –C1	1.717(10)	C18 –C51	1.507(13)
C1 –C2	1.446(13)	C19 –C20	1.448(13)
C1 –C20	1.327(13)	C20 –Cl8	1.710(10)
C2 –N1	1.373(11)	C21 –C22	1.359(14)
C2 –C3	1.411(13)	C21 –C26	1.400(13)
N1 –C19	1.385(11)	C22 –C23	1.404(16)
C3 –C4	1.385(13)	C22 –F22	1.350(13)
C3 –C21	1.510(13)	C23 –C24	1.354(16)
C4 –N2	1.368(11)	C23 –F23	1.335(13)
C4 –C5	1.444(13)	C24 –C25	1.334(16)
N2 –C7	1.384(12)	C24 –F24	1.336(13)
C5 –Cl2	1.724(10)	C25 –C26	1.377(14)
C5 –C6	1.340(14)	C25 –F25	1.341(12)
C6 –Cl3	1.705(11)	C26 –F26	1.338(11)
C6 –C7	1.437(14)	C31 –C32	1.376(15)
C7 –C8	1.398(13)	C31 –C36	1.363(15)
C8 –C9	1.396(13)	C32 –C33	1.384(16)
C8 –C31	1.489(14)	C32 –F32	1.342(12)
C9 –N3	1.393(12)	C33 –C34	1.378(16)
C9 –C10	1.452(14)	C33 –F33	1.349(13)
N3 –C12	1.374(12)	C34 –C35	1.354(16)
C10 –Cl4	1.714(10)	C34 –F34	1.336(14)
C10 –C11	1.349(14)	C35 –C36	1.345(16)
C11 –Cl5	1.710(10)	C35 –F35	1.324(13)
C11 –C12	1.456(13)	C36 –F36	1.341(13)
C12 –C13	1.398(13)	C41 –C42	1.370(15)
C13 –C14	1.400(13)	C41 –C46	1.391(15)
C13 –C41	1.493(13)	C42 –C43	1.393(18)
C14 –N4	1.379(11)	C42 –F42	1.321(14)
C14 –C15	1.455(13)	C43 –C44	1.37(2)
N4 –C17	1.365(11)	C43 –F43	1.352(16)

Table 4. (Cont.)

		Distance(Å)			Distance(Å)
C44	–C45	1.33(2)	C91C	–C92C	1.528
C44	–F44	1.347(18)	C92C	–C93C	1.507
C45	–C46	1.382(19)	C93C	–C94C	1.461
C45	–F45	1.345(17)	C94C	–C95C	1.524
C46	–F46	1.367(14)	C95C	–C96C	1.520
C51	–C52	1.402(15)	C71	–H71A	0.953
C51	–C56	1.384(15)	C71	–H71B	0.948
C52	–C53	1.365(16)	C71	–H71C	0.957
C52	–F52	1.340(13)	C73	–H73A	0.938
C53	–C54	1.333(18)	C73	–H73B	0.947
C53	–F53	1.338(14)	C74	–H74A	0.959
C54	–C55	1.360(18)	C74	–H74B	0.993
C54	–F54	1.333(15)	C74	–H74C	0.890
C55	–C56	1.387(17)	C81	–H81A	0.950
C55	–F55	1.351(15)	C81	–H81B	0.950
C56	–F56	1.323(13)	C81	–H81C	0.950
C61	–O61	1.134(13)	C83	–H83A	0.950
C71	–C72	1.52(2)	C83	–H83B	0.950
C72	–O2	1.213(19)	C84	–H84A	0.950
C72	–O3	1.331(19)	C84	–H84B	0.950
O3	–C73	1.44(3)	C84	–H84C	0.950
C73	–C74	1.39(5)	C91A	–H91A	0.950
C81	–C82	1.535	C91A	–H91B	0.950
C82	–O4	1.191	C91A	–H91C	0.950
C82	–O5	1.490	C92A	–H92A	0.950
O5	–C83	1.411	C92A	–H92B	0.950
C83	–C84	1.421	C93A	–H93A	0.950
C91A	–C92A	1.503	C93A	–H93B	0.950
C92A	–C93A	1.526	C94A	–H94A	0.950
C93A	–C94A	1.530	C94A	–H94B	0.950
C94A	–C95A	1.512	C95A	–H95A	0.950
C95A	–C96A	1.503	C95A	–H95B	0.950
C91B	–C92B	1.515	C96A	–H96A	0.950
C92B	–C93B	1.539	C96A	–H96B	0.950
C93B	–C94B	1.507	C96A	–H96C	0.950
C94B	–C95B	1.524	C91B	–H91D	0.950
C95B	–C96B	1.494	C91B	–H91E	0.950

Table 4. (Cont.)

	Distance(Å)				Angle(°)
C91B –H91F	0.950	N1	–Ru	–N2	89.3(3)
C92B –H92D	0.950	N1	–Ru	–N3	178.8(3)
C92B –H92E	0.950	N1	–Ru	–N4	90.4(3)
C93B –H93D	0.950	N1	–Ru	–C61	91.6(4)
C93B –H93E	0.950	N1	–Ru	–O1	89.2(3)
C94B –H94D	0.950	N2	–Ru	–N3	90.3(3)
C94B –H94E	0.950	N2	–Ru	–N4	172.2(3)
C95B –H95D	0.950	N2	–Ru	–C61	96.4(4)
C95B –H95E	0.950	N2	–Ru	–O1	85.9(3)
C96B –H96D	0.950	N3	–Ru	–N4	89.8(3)
C96B –H96E	0.950	N3	–Ru	–C61	89.6(4)
C96B –H96F	0.950	N3	–Ru	–O1	89.7(3)
C91C –H91G	0.950	N4	–Ru	–C61	91.4(4)
C91C –H91H	0.950	N4	–Ru	–O1	86.3(3)
C91C –H91I	0.950	C61	–Ru	–O1	177.6(4)
C92C –H92G	0.950	Ru	–C61	–O61	178.9(9)
C92C –H92H	0.950	Ru	–N1	–C2	125.7(6)
C93C –H93G	0.950	Ru	–N1	–C19	125.6(6)
C93C –H93H	0.950	Ru	–N2	–C4	125.8(6)
C94C –H94G	0.950	Ru	–N2	–C7	125.2(6)
C94C –H94H	0.950	Ru	–N3	–C9	125.0(6)
C95C –H95G	0.950	Ru	–N3	–C12	125.2(6)
C95C –H95H	0.950	Ru	–N4	–C14	125.6(6)
C96C –H96G	0.950	Ru	–N4	–C17	125.7(6)
C96C –H96H	0.950	C2	–C1	–Cl1	128.7(7)
C96C –H96I	0.950	C20	–C1	–Cl1	122.5(7)
		C20	–C1	–C2	108.4(8)
		N1	–C2	–C1	107.9(7)
		C3	–C2	–C1	127.9(8)
		C3	–C2	–N1	123.7(8)
		C19	–N1	–C2	107.9(7)
		C4	–C3	–C2	126.2(8)
		C21	–C3	–C2	116.6(8)
		C21	–C3	–C4	117.3(8)
		N2	–C4	–C3	125.5(8)
		C5	–C4	–C3	126.5(8)
		C5	–C4	–N2	107.9(8)

Table 4. (Cont.)

	Angle(°)		Angle(°)
C7 –N2 –C4	108.1(7)	C17 –C16 –C15	108.6(9)
Cl2 –C5 –C4	129.5(7)	C17 –C16 –Cl7	130.4(8)
C6 –C5 –C4	108.2(8)	C16 –C17 –N4	108.1(8)
C6 –C5 –Cl2	122.0(8)	C18 –C17 –N4	124.8(8)
Cl3 –C6 –C5	122.6(8)	C18 –C17 –C16	127.0(8)
C7 –C6 –C5	107.7(9)	C19 –C18 –C17	126.8(8)
C7 –C6 –Cl3	129.6(8)	C51 –C18 –C17	115.7(8)
C6 –C7 –N2	108.0(8)	C51 –C18 –C19	117.4(8)
C8 –C7 –N2	125.3(8)	C18 –C19 –N1	124.6(8)
C8 –C7 –C6	126.4(9)	C20 –C19 –N1	107.8(7)
C9 –C8 –C7	125.7(9)	C20 –C19 –C18	127.7(8)
C31 –C8 –C7	117.5(8)	C19 –C20 –C1	107.9(8)
C31 –C8 –C9	116.8(8)	Cl8 –C20 –C1	122.7(7)
N3 –C9 –C8	125.7(8)	Cl8 –C20 –C19	129.2(7)
C10 –C9 –C8	127.4(9)	C22 –C21 –C3	122.9(9)
C10 –C9 –N3	106.9(8)	C26 –C21 –C3	121.1(8)
C12 –N3 –C9	108.9(7)	C26 –C21 –C22	116.0(9)
Cl4 –C10 –C9	129.5(8)	C23 –C22 –C21	122.1(10)
C11 –C10 –C9	108.7(9)	F22 –C22 –C21	118.2(9)
C11 –C10 –Cl4	121.7(8)	F22 –C22 –C23	119.7(9)
Cl5 –C11 –C10	122.2(8)	C24 –C23 –C22	119.4(10)
C12 –C11 –C10	107.5(9)	F23 –C23 –C22	119.0(10)
C12 –C11 –Cl5	130.3(7)	F23 –C23 –C24	121.6(10)
C11 –C12 –N3	108.0(8)	C25 –C24 –C23	120.1(11)
C13 –C12 –N3	125.2(8)	F24 –C24 –C23	117.9(10)
C13 –C12 –C11	126.6(9)	F24 –C24 –C25	122.0(10)
C14 –C13 –C12	125.2(8)	C26 –C25 –C24	121.0(10)
C41 –C13 –C12	117.2(8)	F25 –C25 –C24	120.1(10)
C41 –C13 –C14	117.5(8)	F25 –C25 –C26	119.0(9)
N4 –C14 –C13	125.7(8)	C25 –C26 –C21	121.4(9)
C15 –C14 –C13	126.1(8)	F26 –C26 –C21	119.6(8)
C15 –C14 –N4	108.2(8)	F26 –C26 –C25	119.0(9)
C17 –N4 –C14	108.2(7)	C32 –C31 –C8	120.9(9)
Cl6 –C15 –C14	129.2(7)	C36 –C31 –C8	122.8(9)
C16 –C15 –C14	106.8(9)	C36 –C31 –C32	116.3(10)
C16 –C15 –Cl6	123.6(8)	C33 –C32 –C31	121.3(10)
Cl7 –C16 –C15	120.9(8)	F32 –C32 –C31	120.4(9)

Table 4. (Cont.)

	Angle(°)				Angle(°)
F32 –C32 –C33	118.2(9)	C54	–C53	–C52	120.2(11)
C34 –C33 –C32	119.1(11)	F53	–C53	–C52	120.0(11)
F33 –C33 –C32	119.5(10)	F53	–C53	–C54	119.8(11)
F33 –C33 –C34	121.3(10)	C55	–C54	–C53	120.3(12)
C35 –C34 –C33	119.9(11)	F54	–C54	–C53	121.3(11)
F34 –C34 –C33	118.2(10)	F54	–C54	–C55	118.3(11)
F34 –C34 –C35	121.9(10)	C56	–C55	–C54	121.5(11)
C36 –C35 –C34	119.4(11)	F55	–C55	–C54	121.2(11)
F35 –C35 –C34	117.6(10)	F55	–C55	–C56	117.3(11)
F35 –C35 –C36	123.0(10)	C55	–C56	–C51	118.9(10)
C35 –C36 –C31	123.9(10)	F56	–C56	–C51	119.6(10)
F36 –C36 –C31	118.5(9)	F56	–C56	–C55	121.5(10)
F36 –C36 –C35	117.6(10)	O2	–C72	–C71	124.5(15)
C42 –C41 –C13	123.3(9)	O3	–C72	–C71	113.1(14)
C46 –C41 –C13	119.4(9)	O3	–C72	–O2	122.2(14)
C46 –C41 –C42	117.3(10)	C73	–O3	–C72	119.2(16)
C43 –C42 –C41	120.1(11)	C74	–C73	–O3	113.0(26)
F42 –C42 –C41	120.4(10)	O4	–C82	–C81	115.5
F42 –C42 –C43	119.5(11)	O5	–C82	–C81	134.5
C44 –C43 –C42	120.8(13)	O5	–C82	–O4	108.6
F43 –C43 –C42	118.8(12)	C83	–O5	–C82	122.2
F43 –C43 –C44	120.3(12)	C84	–C83	–O5	111.7
C45 –C44 –C43	120.0(14)	C93A –C92A –C91A			110.7
F44 –C44 –C43	121.0(13)	C94A –C93A –C92A			109.7
F44 –C44 –C45	119.0(13)	C95A –C94A –C93A			111.0
C46 –C45 –C44	119.9(13)	C96A –C95A –C94A			112.0
F45 –C45 –C44	119.8(13)	C93B –C92B –C91B			110.5
F45 –C45 –C46	120.3(12)	C94B –C93B –C92B			111.8
C45 –C46 –C41	121.8(11)	C95B –C94B –C93B			111.5
F46 –C46 –C41	119.4(10)	C96B –C95B –C94B			111.1
F46 –C46 –C45	118.8(11)	C93C –C92C –C91C			113.1
C52 –C51 –C18	121.2(9)	C94C –C93C –C92C			114.3
C56 –C51 –C18	121.1(9)	C95C –C94C –C93C			111.8
C56 –C51 –C52	117.7(9)	C96C –C95C –C94C			111.9
C53 –C52 –C51	121.4(10)	H71A –C71	–C72		109.9
F52 –C52 –C51	119.2(9)	H71B –C71	–C72		110.1
F52 –C52 –C53	119.4(10)	H71C –C71	–C72		109.6

Table 4. (Cont.)

			Angle(°)				Angle(°)
H71B	–C71	–H71A	109.4	H92A	–C92A	–C91A	109.2
H71C	–C71	–H71A	108.7	H92B	–C92A	–C91A	109.2
H71C	–C71	–H71B	109.1	H92A	–C92A	–C93A	109.2
H73A	–C73	–O3	109.9	H92B	–C92A	–C93A	109.2
H73B	–C73	–O3	109.3	H92B	–C92A	–H92A	109.5
H73A	–C73	–C74	109.4	H93A	–C93A	–C92A	109.4
H73B	–C73	–C74	104.4	H93B	–C93A	–C92A	109.4
H73B	–C73	–H73A	110.7	H93A	–C93A	–C94A	109.4
H74A	–C74	–C73	107.9	H93B	–C93A	–C94A	109.4
H74B	–C74	–C73	105.6	H93B	–C93A	–H93A	109.5
H74C	–C74	–C73	112.7	H94A	–C94A	–C93A	109.1
H74B	–C74	–H74A	105.3	H94B	–C94A	–C93A	109.1
H74C	–C74	–H74A	114.0	H94A	–C94A	–C95A	109.1
H74C	–C74	–H74B	110.8	H94B	–C94A	–C95A	109.1
H81A	–C81	–C82	109.5	H94B	–C94A	–H94A	109.5
H81B	–C81	–C82	109.5	H95A	–C95A	–C94A	108.8
H81C	–C81	–C82	109.5	H95B	–C95A	–C94A	108.8
H81B	–C81	–H81A	109.5	H95A	–C95A	–C96A	108.8
H81C	–C81	–H81A	109.5	H95B	–C95A	–C96A	108.8
H81C	–C81	–H81B	109.5	H95B	–C95A	–H95A	109.5
H83A	–C83	–O5	108.9	H96A	–C96A	–C95A	109.5
H83B	–C83	–O5	108.9	H96B	–C96A	–C95A	109.5
H83A	–C83	–C84	108.9	H96C	–C96A	–C95A	109.5
H83B	–C83	–C84	108.9	H96B	–C96A	–H96A	109.5
H83B	–C83	–H83A	109.5	H96C	–C96A	–H96A	109.5
H84A	–C84	–C83	109.5	H96C	–C96A	–H96B	109.5
H84B	–C84	–C83	109.5	H91D	–C91B	–C92B	109.5
H84C	–C84	–C83	109.5	H91E	–C91B	–C92B	109.5
H84B	–C84	–H84A	109.5	H91F	–C91B	–C92B	109.5
H84C	–C84	–H84A	109.5	H91E	–C91B	–H91D	109.5
H84C	–C84	–H84B	109.5	H91F	–C91B	–H91D	109.5
H91A	–C91A	–C92A	109.5	H91F	–C91B	–H91E	109.5
H91B	–C91A	–C92A	109.5	H92D	–C92B	–C91B	109.2
H91C	–C91A	–C92A	109.5	H92E	–C92B	–C91B	109.2
H91B	–C91A	–H91A	109.5	H92D	–C92B	–C93B	109.2
H91C	–C91A	–H91A	109.5	H92E	–C92B	–C93B	109.2
H91C	–C91A	–H91B	109.5	H92E	–C92B	–H92D	109.5

Table 4. (Cont.)

	Angle(°)			Angle(°)
H93D –C93B –C92B	108.9		H94H –C94C –C93C	108.9
H93E –C93B –C92B	108.9		H94G –C94C –C95C	108.9
H93D –C93B –C94B	108.9		H94H –C94C –C95C	108.9
H93E –C93B –C94B	108.9		H94H –C94C –H94G	109.5
H93E –C93B –H93D	109.5		H95G –C95C –C94C	108.9
H94D –C94B –C93B	108.9		H95H –C95C –C94C	108.9
H94E –C94B –C93B	108.9		H95G –C95C –C96C	108.9
H94D –C94B –C95B	108.9		H95H –C95C –C96C	108.9
H94E –C94B –C95B	108.9		H95H –C95C –H95G	109.5
H94E –C94B –H94D	109.5		H96G –C96C –C95C	109.5
H95D –C95B –C94B	109.1		H96H –C96C –C95C	109.5
H95E –C95B –C94B	109.1		H96I –C96C –C95C	109.5
H95D –C95B –C96B	109.1		H96H –C96C –H96G	109.5
H95E –C95B –C96B	109.1		H96I –C96C –H96G	109.5
H95E –C95B –H95D	109.5		H96I –C96C –H96H	109.5
H96D –C96B –C95B	109.5			
H96E –C96B –C95B	109.5			
H96F –C96B –C95B	109.5			
H96E –C96B –H96D	109.5			
H96F –C96B –H96D	109.5			
H96F –C96B –H96E	109.5			
H91G –C91C –C92C	109.5			
H91H –C91C –C92C	109.5			
H91I –C91C –C92C	109.5			
H91H –C91C –H91G	109.5			
H91I –C91C –H91G	109.5			
H91I –C91C –H91H	109.5			
H92G –C92C –C91C	108.6			
H92H –C92C –C91C	108.6			
H92G –C92C –C93C	108.6			
H92H –C92C –C93C	108.6			
H93G –C93C –C92C	108.3			
H93H –C93C –C92C	108.3			
H93G –C93C –C94C	108.3			
H93H –C93C –C94C	108.3			
H93H –C93C –H93G	109.5			
H94G –C94C –C93C	108.9			

**Table 5. Intermolecular Distances Less Than 3.5 Å for
Aquo, Carbonyl Tetrakis(Pentafluorophenyl)octachloroporphyrin Ruthenium(II).**

	Distance(Å)		Distance(Å)
Cl1 −F25	3.140(7)	F23 −F36	3.411(10)
C1 −F43	3.423(12)	F24 −F53	3.439(10)
N1 −F43	3.353(11)	F24 −F54	2.981(10)
C4 −O4	3.436	F24 −F44	3.359(11)
N2 −F33	3.415(10)	F24 −F35	3.036(10)
N3 −O2	3.250(13)	F24 −F25	3.314(9)
Cl4 −C91B	3.460	F24 −F26	3.378(9)
Cl4 −F25	3.152(7)	F25 −F53	2.862(10)
C18 −F43	3.471(12)	F25 −F25	3.264(9)
C19 −F43	2.998(12)	F26 −F33	2.982(9)
C20 −F43	3.057(12)	F26 −F34	3.080(9)
C23 −F54	3.191(13)	F32 −C71	3.249(19)
C24 −F53	3.400(14)	F32 −C72	3.057(17)
C24 −F54	3.039(13)	F32 −O2	3.422(12)
C24 −F25	3.087(13)	F32 −O3	3.208(13)
C25 −F53	3.140(13)	F32 −C74	3.47(4)
C25 −C25	3.417(15)	F32 −C91A	3.283
C25 −F25	3.060(12)	F33 −C91A	3.203
C33 −F26	3.032(13)	F33 −C92A	3.353
C34 −F26	3.100(13)	F33 −C61	3.369(12)
C35 −F24	3.394(13)	F33 −O61	3.176(11)
C43 −F34	3.246(15)	F34 −F43	3.170(11)
C44 −F34	3.189(17)	F34 −F44	3.088(11)
C44 −F35	3.409(17)	F34 −O61	3.035(11)
C45 −F35	3.300(16)	F35 −F44	3.400(11)
C54 −F45	3.104(16)	F35 −F45	3.169(11)
C55 −C96A	3.456	F35 −C71	3.442(19)
C55 −F45	3.157(15)	F35 −O3	3.367(13)
C56 −C96A	3.444	F36 −O3	3.323(13)
F22 −C81	3.490	F36 −C91A	2.576
F22 −C82	3.154	F36 −C91B	2.652
F22 −O5	3.004	F36 −C91C	3.022
F23 −F54	3.296(10)	F42 −F52	3.318(10)
F23 −C91A	3.083	F43 −F52	3.033(11)
F23 −C91B	2.409	F43 −C61	3.362(13)
F23 −C91C	2.711	F43 −O61	3.170(12)
F23 −F35	3.491(10)	F45 −F54	3.013(12)

Table 5. (Cont.)

Distance(Å)

F45 –F55	3.174(12)
F45 –C96A	3.393
F46 –C95A	3.328
F46 –C96A	3.253
F46 –C95B	3.230
F46 –C96B	3.465
F46 –C95C	3.214
F52 –C74	3.47(4)
F55 –C96A	2.975
F55 –C96B	3.448
F55 –C96C	3.228
F55 –C71	3.47(2)
F55 –C81	3.245
F55 –C82	3.305
F55 –O4	3.449
F56 –C81	3.428
F56 –C96A	3.017
O61 –C92A	3.305
O61 –C92C	3.389
O1 –C81	3.210
O1 –C82	3.371
O1 –O4	2.668
O1 –C96C	3.362
O1 –O2	2.683(12)
O2 –C96C	3.306
O4 –C83	3.060
O5 –O5	3.309
O5 –C84	2.343
C84 –C84	2.453

Table 6. Observed and Calculated Structure Factors for

Aquo, Carbonyl Tetrakis(pentafluorophenyl)porphyrin Ruthenium(II)

The columns contain, in order, ℓ, $10F_{obs}$, $10F_{calc}$ and $10\sigma F_{obs}$. A minus sign preceding F_{obs} indicates that F_{obs}^2 is negative.

Aquo. Carbonyl Tetrakis(pentafluorophenyl)octachloroporphyrin Ru(II)   Page 1

```
-15  0  1          3  715  697  18     -13  2  1            9   72   66  59      9 -147   92  29      9  253  252  25
                   4  863  866  18                         10  794  773  18     10 -126  112  34     10  396  387  20
2  893  807  26    5  762  743  18     1  785  759  17     11  405  409  21     11  278  300  23     11  150  195  36
4  347  396  32    6   87  109  51     2  389  339  20                          12  257  233  24     12  503  488  19
6  424  432  30    7  197  146  30     3 1205 1179  18     -13  7  1            13  313  316  22     13  217  267  29
                   8  194  122  31     4  406  444  19                          14  225  230  27     14  -52   84  68
-15  1  1          9 1018  994  19     5  215  114  27     1  205  155  29      15  111  137  44     15  148  222  39
                  10  247  253  27     6  292  264  23     2  248  257  26      16  531  522  19
1  433  380  21   11  237  266  28     7  330  316  21     3  -29   75  81      17  614  587  19     -12  7  1
2  879  871  19                        8   78  163  52     4  181  237  32
3  427  440  21    -14  4  1            9  391  413  20     5  123   23  42      -12  3  1           1  147  167  35
4  383  358  22                       10  493  517  19     6  571  556  19                          2   51   26  64
5  547  531  20    1  335  336  22    11  228  197  27     7   24   62  87      1 -135   50  30      3  232  261  26
6  504  495  20    2  321  347  23    12   79  136  54     8  514  441  20      2  321  309  20      4  432  392  19
                   3  277  229  25    13  -17   19  91     9   92   27  52      3  985 1035  17      5  -49   47  65
-15  2  1          4  208  126  29    14  464  443  20    10  267  237  27      4  602  620  17      6  543  487  18
                   5  282  255  24    15  790  766  19                          5  -91   64  43      7  147  119  36
1   41   25  75    6  176    7  33                         -13  8  1            6  563  575  17      8  945  886  18
2  -74   23  56    7  648  672  19     -13  3  1                                7  184  202  29      9  223   96  28
3  507  479  20    8  300  281  24                         1  223  183  28      8  452  450  18     10  543  523  19
4  404  373  21    9  345  326  23     1  383  344  20     2  470  491  20      9  513  551  18     11  305  288  24
5  418  405  21   10  150  201  38     2  390  390  20     3  229  207  28     10 -176   34  24     12  160  160  36
6  227  259  29                        3  268  179  24     4  399  466  21     11 -185   27  23     13  269  242  26
                   -14  5  1            4  187    4  29     5  143  196  39     12  -85   58  48
-15  3  1                               5  945  930  17     6   76  108  58     13  193  176  30     -12  8  1
                   1  107    0  46     6  380  400  20     7  146  131  39     14  140  121  37
1  608  584  19    2  911  B70  18     7  113  133  42     8   62   37  65     15  752  755  18     1  470  441  19
2  127   58  43    3  694  705  18     8  -76   42  51                         16  148  112  37     2  369  309  21
3  417  424  21    4  650  608  18     9  156   66  34     -13  9  1           17  279  156  26     3  355  365  21
4  179  108  34    5  325  341  23    10  459  385  19                                              4  439  438  20
                   6  451  495  20    11  760  760  18     1  472  444  20      -12  4  1           5  210  112  29
-15  4  1          7  126   55  42    12  106  133  46     2  195  188  32                          6  797  803  18
                   8  735  663  19    13  481  515  20     3 -156   77  31      1  526  550  17      7  295  285  24
1  170   77  35                       14  458  438  20     4   84    7  55      2  466  433  18      8  196  178  31
                   -14  6  1                                                    3  372  327  19      9  438  377  20
-14  0  1                               -13  4  1          -12  0  1            4  399  408  19     10  683  713  19
                   1  489  514  20                                              5  437  492  18     11  214  140  30
2  663  641  25    2   39   71  76     1  278  281  23     2  222  218  40      6   35  139  73     12  364  379  23
4  170  231  45    3   69   24  60     2  349  326  21     4 -229   18  22      7  422  373  19
6  897  867  25    4  165  201  35     3  664  655  17     6 1027 1071  23      8  232  235  25      -12  9  1
8  179  205  44    5  -43   42  73     4  140  131  36     8 -112  115  50      9  -59   18  59
10  631  579  26   6  459  466  21     5  277  260  23    10 -207    6  27     10  196  117  29      1  151   55  36
12  600  555  27   7  366  335  22     6  238  243  26    12  808  773  24     11  372  378  20      2  224  255  28
                                       7  235  220  26    14  663  568  25     12  293  325  23      3  178  188  32
-14  1  1          -14  7  1            8  519  445  19    16  462  422  28     13  563  549  18      4  374  312  21
                                       9  906  911  18    18  287  340  35     14 -139   64  33      5   94   62  50
1  246  217  26    1  222  157  29    10  151   70  36                         15  154  108  36      6  389  425  21
2  523  485  19    2  550  537  19    11  359  393  22     -12  1  1           16  262  261  26      7  386  356  22
3  153  195  35    3  422  360  21    12 -124    2  38                                               8  426  427  21
4  304  293  23                       13  355  337  23     1   84   77  53      -12  5  1           9  559  556  20
5   67   80  58    -13  0  1           14  433  420  21     2  320  402  24                         10  157   10  38
6  608  574  18                                            3 -166   21  28     1 -113  138  37
7  242  157  26    2 1663 1611  26     -13  5  1            4  293  374  21     2   86   27  48      -12 10  1
8  711  719  18    4  537  544  25                         5   99  171  43     3  514  516  18
9  301  271  24    6  216  157  37     1 -155   24  28     6   68  127  54      4  453  476  18      1  355  296  22
10  337  298  23   8  262  310  34     2  120  203  40     7  405  378  19      5   74   88  53      2  202  145  31
11  234  169  28   10  79    8  69     3  321  301  22     8 -122  125  34      6  309  239  22      3  110   84  46
12 -155   38  31   12  531  529  26     4  -66   27  56     9 -115   21  36      7  931  879  17      4  182  146  33
                   14  963  972  25     5  189  262  30    10  257  315  24      8  527  496  18      5  743  724  19
-14  2  1                               6  360  355  21    11  127  167  38      9  811  785  17      6  231  154  29
                   -13  1  1            7  456  418  19    12  270  243  23     10  140  163  37      7  677  568  19
1   80   89  53                         8  271  250  25    13   85   78  50     11  -72   11  54
2  189  204  30    1  548  503  18     9  235  205  27    14  800  746  18     12  399  389  20      -11  0  1
3  249  263  26    2  699  657  17    10  247  265  27    15  419  370  20     13  180  151  32
4  144   54  37    3  193  118  29    11  -92   66  48    16  654  654  18     14  431  386  20      2 1295 1283  26
5  548  521  19    4  835  757  17    12  490  529  20    17  294  299  24     15  694  702  19      4  536  490  26
6  434  396  20    5 1153 1104  18    13  716  750  19    18  255  206  27     16  470  436  20      6 -183  112  32
7  540  507  19    6  799  725  17                                                                  8  455  547  28
8  351  383  22    7  268  280  24     -13  6  1          -12  2  1             -12  6  1           10  508  466  24
9  250  252  26    8 -127   85  34                                                                 12  762  748  23
10  164   44  35   9 -119  100  36     1 -127   24  35    1  117  222  41      1  354  324  20     14  788  760  24
11  722  695  19   10  205  173  28     2  121  236  41    2 -131   87  31      2 -189   53  22     16  390  466  28
                   11  696  607  18     3 -129   70  34    3  187  196  28      3  -10  144  93     18  201  258  42
-14  3  1          12  917  852  18     4  315  296  22    4  -95   51  41      4 -126   47  34     20  638  603  27
                   13   85   35  52     5  -47   74  68    5  650  686  17      5  481  503  18
1  600  610  18    14  186   27  32     6  -73   67  54    6  227  234  25      6  415  396  19      -11  1  1
2  132  108  39    15  256  170  27     7  143   45  37    7  519  528  17      7  233  208  26
                                        8  510  516  19    8 -117    1  36      8  -67   47  56      1 -113   24  38
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Aquo. Carbonyl Tetrakis(pentafluorophenyl)octachloroporphyrin Ru(II)   Page 2

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 2   51   99  65     13  563  562  18      9  369  325  21     10   97  148  46     16 -142  125  31      5  625  572  17
 3  -58  139  60     14   28  123  79     10  249  285  26     11  402  445  21     17  332  397  22      6  452  482  18
 4  830  744  18     15  155  245  35     11  298  255  24     12  455  418  20     18  235  277  27      7  202  225  28
 5  166  260  33     16 -156   47  29     12  -75   63  55     13  244  240  23     19   58   97  64      8  140  162  36
 6  573  572  19     17 -174   34  27     13  201  138  31     14  879  901  17     20  -21  108  90      9  640  652  17
 7   52  178  65     18  112  131  45     14  464  465  20     15  128  142  37                          10  -37   22  73
 8  -85   57  49     19  299  276  25     15  153  143  38     16 -123   35  35     -10   5   1           11 -145   32  31
 9 -176    1  25                                              17 -137   70  32                          12  255  249  25
10  561  601  17     -11   5   1          -11   9   1         18 -134   93  33      1   83  121  50      13  152  194  35
11  601  590  17                                              19  176  227  32      2  810  810  18      14  -74    8  55
12  182  249  29      1  427  412  21      1  605  609  18     20  632  639  19      3  591  600  18      15  111  126  45
13  335  339  20      2  151    6  36      2  153   96  34     21  449  454  20      4   53   18  64      16  355  376  22
14 -141   35  30      3 1008 1030  19      3  136  233  37                           5  525  526  19      17 -146  117  34
15  337  351  21      4  178  207  33      4  128   91  39     -10   2   1           6 -192   66  22
16  538  523  18      5  156  117  31      5  -65   38  57                           7  190  304  31      -10   9   1
17 -174   49  26      6  797  785  16      6 -156   90  29      1  322  331  21       8  -75   13  54
18  237  293  27      7  286  358  22      7  412  377  20      2  143   57  33       9   95   95  49      1  -97   11  42
19  -51   41  68      8  522  558  17      8  -30   42  80      3 1529 1480  20      10  -95   32  41      2  219  140  26
20  167  130  36      9  321  256  21      9  282  263  25      4  414  393  19      11  -89   72  44      3  673  663  17
                     10  408  394  19     10  178  255  33      5  909  871  18      12   94  103  46      4 -112  103  38
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 5  595  645  19                                               10 -135   26  33     18 -140   81  34     14 -135    3  37
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  1   53  119  70        6  682  627  17       10  157   70  36      -9 10  1           1 1135 1158  16       24  237  249  29
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 17  475  538  18       17   62   79  59       -9  8  1              -9 12  1            10 1245 1260  18       7  153  102  31
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-8  7  1              7  -31   25  75     8  989  935  21    11  716  692  16     7  112  132  37    10  146  155  38
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Aquo. Carbonyl Tetrakis(pentafluorophenyl)octachloroporphyrin Ru(II)   Page 7

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 3  360  416 17      4  455  431 19      3  176  187 32     16  816  825 16      2 1067 1059 13     21  478  522 18
 4  977  911 16      5  282  299 23      4  210  185 28     17  115  129 36      3  380  383 13     22  322  338 22
 5 1533 1568 19      6  296  308 23      5  247  296 26     18  271  267 22      4 2124 2167 20     23  225  263 27
 6  507  505 16      7  486  496 19      6  258  241 25     19  -90   41 44      5 1266 1253 15     24  415  396 20
 7  260  126 20      8  511  539 19      7  370  356 21     20  383  405 21      6  971  921 14     25  110  106 46
 8   25    4 71      9  460  488 20      8  -84   21 51     21  904  910 19      7  305  325 15     26  217  258 30
 9  418  451 18     10  164  195 29      9  197  178 31     22  346  309 23      8 1056 1109 15
10  284  296 21     11  184  246 28                         23   44  148 68      9  738  707 14        -1  8  1
11  299  336 21     12  403  409 19        -2 17  1         24  287  338 23     10  113   20 30
12  -58  121 57     13  535  527 17                         25  407  416 20     11  778  802 15      1  244  331 18
13  379  390 20     14   22    4 82      1  109   15 45     26  284  252 24     12  367  418 17      2  400  340 15
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20  189  196 30      4  162   23 31     13  418  373 15                         16 1272 1236 19      8  226  179 22
21  410  322 21      5  -85   39 45     14  794  732 15        -1  4  1         17  629  593 18      9  693  694 16
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                    10  150   14 34     19  212  229 27      4  498  447 12     22 -154   29 29     14  325  405 22
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10  136   21 37      1  160  121 32                         14  523  520 16      3  384  401 14     24  207  193 31
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12  176   64 33      3  241  239 25                         16  376  370 18      5 1072 1110 15        -1 10  1
13  -28   69 75      4  366  313 20      1  417  745  9     17  973  914 17      6 1952 1986 20
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15  462  408 18      6  -57   23 60      3  424  346 10     19  125  162 39      8  945  897 15      2  390  397 17
16  -17  143 87      7  314  320 22      4  157   21 20     20  105   93 46      9  423  377 16      3  600  636 16
17 -105   24 41      8  251  243 25      5  901  620 11     21  406  432 22     10  830  780 15      4  214   81 23
18  491  471 19      9  345  281 21      6 1082  960 13     22  -99   21 41     11  663  594 16      5  561  516 16
19  269  248 25     10  278  347 24      7  527  438 12     23  124  208 39     12   32   33 66      6   76  131 46
20  100  120 48     11  406  405 20      8  -58   80 41     24  565  575 18     13  -83   27 41      7  335  399 19
21  370  330 22     12  125  111 41      9 2986 2977 27     25  257  293 25     14  969  957 17      8  -98   65 37
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   -2 12  1                             11  -24  114 64     27  107  143 48     16  -25   95 79     10  209  143 26
                       -2 16  1         12  791  709 14                         17  204  177 29     11  626  586 18
 1  158   66 32                         13  361  308 16        -1  5  1         18  650  645 19     12  192  166 29
 2  569  586 18      1  490  434 19     14  -51   55 52                         19 -122   62 38     13  -56   97 61
 3  176   72 30      2  143   44 36     15 1357 1354 18      1  850  916 12     20 -162   27 26     14 -152   98 29
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15  407  390  21              -1 14  1         3   215  231  13       18  503  448  18       3 1974 1997  20       22  113  158  43
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22  157   87  36          6 -133   18  31      10 1824 1724  19       25  216  153  28      10 1174 1169  16       1  682  684  15
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5  335  322  20          15  283  287  24      19  230   39  25       2 2025 2015  19       19  -74   61  54      10  548  504  17
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7  736  733  17                                21  674  598  19       4  420  449  12       21  446  473  18      12  335  361  20
8  225  314  26             -1 15  1           22 1018  966  19       5 1845 1799  18       22  253  276  24      13  746  755  17
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12  139  252  37          3  110   35  41      26  179  183  32       9 1319 1264  16       26  413  428  21      17  547  577  17
13  255  256  26          4 -116    9  36      27  396  369  21      10  -65   98  40                             18  119  120  39
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15   70   97  53          6  219  121  26                            12   97  136  35                             20  126  196  39
16  327  364  21          7  420  308  19          0  2  1           13 1432 1399  18       1  432  523  14       21  374  340  21
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18  -22   48  84          9  172  151  32       0 1779 1968  16       15  332  315  18       3  726  741  13       23  155  199  36
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21 -169    7  28          12  205  243  29      3  682  326   9       18 1021  985  18       6  965  937  15          0 10  1
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                          14  299  213  36      5 2721 2573  19       20  199  181  30       8 1371 1483  17       0  415  439  16
   -1 12  1                                     6   50    4  45       21  307  305  24       9  420  477  16       1  618  589  16
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1  138  113  35                                 8 1661 1625  17       23  793  758  17      11  261  255  20       3  265  300  20
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4  113  160  40          3  565  577  18       11 1425 1393  17       26  169  141  34      14  584  638  17       6  270  276  21
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7  134  143  37          6   71  157  57       14  292  290  18          0  5  1            17  -52   89  63       9   72   71  50
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9  512  529  19          8  189  154  31       16  925  924  16       1 1238 1370  14       19 -145   46  32      11  894  927  18
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12   45   85  64                                19 1612 1579  21       4 1349 1417  15       22  671  689  17      14  528  575  19
13  143   77  34            -1 17  1            20  361  290  21       5  319  357  14       23  156   84  35      15  258  318  26
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16  190  183  29          2  224  211  28       23  277  279  23       8  522  592  13       26  374  298  23      18 -110   28  38
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   -1 13  1               2  849 1029  11                            14  280  264  20       2  937  977  15
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4  137   83  37         12  910  924  19       3 4866 4883  42       19  315  321  23       7  660  761  15       3  611  525  17
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16  105  197  45          1 1197 1554   -      15  516  539  16       0  265  172  15       19  460  488  18      15  122  121  38
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18  518  391  20                               17  579  603  17       2  123  134  25       21  175   26  31      17  -66  135  54
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18  -38   31  72        6  101  166  44       27 -102   79  45        9  529  484  13       25  130    3  41       14  683  683  18
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22  277  250  26       10  403  351  20                              13  425  430  16                              18  284  321  22
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    0  12  1           12   95   30  49        1  408  182   9       15 1272 1326  18        1  189  220  20       20  317  323  22
                       13  137  155  40        2 1210 1123  12       16  327  277  19        2  147  177  23       21  166  196  33
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 1  454  494  18                               4 1686 1848  16       18  465  442  19        4 2228 2378  22       23  509  494  20
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12  778  810  16        8  -26   67  83       15 1323 1340  18         1   5  1            15  157  110  31        6  336  335  19
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15  135   70  36                               18  154  170  32        1 1460 1504  15       18  410  429  21        9  660  688  17
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19  390  395  21        2  232   64  27       22  636  599  20        5 1797 1793  18       22  333  265  21       13  779  810  18
20  251  312  27        3  305  358  24       23  153  212  34        6  110  168  28       23  151  111  35       14   56   94  62
                        4  201  155  30       24  309  310  22        7  588  606  13       24  583  594  19       15  -94   43  45
    0  13  1                                   25  288  220  24        8  186  207  20       25  263  228  26       16   83   95  47
                           1   0  1            26  605  539  18        9   65   46  41       26  609  596  20       17  317  327  21
 1  282  208  23                               27  415  415  21       10  255  188  18                              18  168  116  31
 2  584  534  18        0  267  203   9        28  333  319  24       11  614  656  14         1   8  1            19  517  563  18
 3  372  410  21        2 2489 2370  25                              12 1612 1648  19                              20  244  234  25
 4  350  327  22        4  198  420  21         1   3  1            13  324  386  18        0  213  211  14       21  458  458  20
 5  173  135  32        6  545  650  15                              14  436  509  17        1 1150 1108  15       22  188   84  32
 6  175  148  32        8  540  681  17        0  289   13   9       15   43  109  61        2  432  366  15       23  219  267  30
 7  194   51  26       10 3374 3287  36        1  870  933  11       16  678  698  17        3  707  792  14
 8  644  702  16       12  168  168  32        2  360  485  12       17 1024 1039  18        4  614  636  14         1  11  1
 9  224  174  25       14  717  685  21        3 1267 1261  13       18  698  691  18        5  331  340  17
10  346  345  20       16 1638 1596  25        4  132    2  23       19  806  803  18        6  309  326  17        0  260  266  15
11  297  323  20       18 1363 1273  25        5  816  839  11       20 -169  122  27        7  730  689  15        1  844  887  17
12  105   58  42       20  842  761  25        6  194  322  18       21  140  163  35        8  935  970  16        2  243  249  22
13  131   51  37       22  938  859  26        7 1579 1459  16       22  691  634  17        9  237  301  21        3  399  428  18
14  419  483  19       24  421  336  27        8 1954 1834  19       23  732  737  17       10  419  405  17        4  636  677  17
15  257  291  24       26  409  388  29        9 -166   23  16       24  198  162  29       11  383  405  18        5  826  786  17
16  267  226  24       28  419  355  30       10  630  661  13       25   63  199  61       12  429  513  17        6  134   48  34
17  244  305  26                              11 1298 1356  16       26   90   93  52       13 -129    1  29        7  242  244  24
18  116   82  44           1   1  1           12  742  721  14       27  168   60  36       14  653  681  17        8  464  525  19
                                              13 1947 1911  21                              15  235  195  25        9  161  108  32
    0  14  1            0 1666 1310  13       14  575  611  15         1   6  1            16  506  490  19       10  180   34  31
                        1  115  256  18       15  277  186  20                              17  582  629  19       11  952 1025  18
 0  323  435  20        2  679  603   9       16  763  768  16        0  461  463   9       18  -25  115  85       12  444  338  20
 1 -161   43  25        3  994  731  11       17  663  655  17        1  602  599  12       19  348  309  20       13  586  547  18
 2  -28   18  74        4  868  799  10       18 -134    1  30        2  854  850  13       20  799  829  17       14  -93   67  41
 3  -12   51  88        5  445  230  11       19  503  492  19        3  201  124  18       21  501  452  18       15  109  111  40
 4  126  110  36        6 2455 2466  22       20 -104   91  42        4 2188 2177  21       22  286  260  23       16  446  480  18
 5   74   47  51        7 1164 1077  13       21  359  358  22        5  330  153  15       23  228  244  28       17  565  548  17
 6  393  353  19        8  571  601  12       22  592  602  17        6  562  527  13       24  235  198  28       18  256  229  24
 7  481  512  18        9  954  913  13       23  330  342  21        7  869  878  14       25  642  602  19       19  456  460  19
 8  140   27  35       10  518  491  13       24 -116   70  38        8  848  886  14                              20  592  593  18
 9  203  148  27       11  831  825  14       25  597  568  18        9  495  534  14         1   9  1           21  164   98  35
10  247  265  25       12 1122 1061  15       26  178  113  33       10  543  535  15
11  156  112  33       13  211  114  21       27  421  389  21       11  496  473  15        0  536  515  11         1  12  1
12  552  518  18       14  594  594  15       28  238  155  29       12 1131 1131  16        1 1500 1485  18
13  252  263  25       15  -77   13  41                              13   70   79  46        2  221  122  20        0  403  429  14
14  159  104  34       16  144   90  30         1   4  1            14  926  982  17        3 1043 1047  16        1 -112   73  36
15  171  232  33       17  709  712  16                              15  415  316  18        4  676  595  15        2  512  495  18
16  218  209  29       18  151  226  32        0 1160 1252  11       16  855  877  17        5 1642 1654  19        3  591  607  18
                       19  368  361  20        1  938 1165  12       17  351  298  21        6 1655 1653  19        4  138   37  35
    0  15  1           20  485  441  19        2 2052 1986  19       18  160  106  34        7  411  462  17        5  138  188  35
                       21  272  281  25        3 4072 3967  35       19  346  345  22        8  384  403  18        6  287  298  23
 1  166   76  31       22  268  164  26        4 1525 1428  16       20  384  398  22        9  370  355  18        7  141   11  36
 2  419  443  19       23  175  190  31        5  733  758  12       21  472  467  18       10   94   88  41        8  545  574  19
 3  344  260  20       24  776  749  17        6  188   19  18       22  815  770  17       11 -127   93  30        9  444  448  20
 4  397  469  19       25  756  713  18        7 2685 2789  25       23  238  285  26       12  188  237  27       10  329  403  23
 5   67   51  55       26  398  367  21        8  904  957  13       24   75  169  55       13  128  159  36       11  153  199  32
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Aquo. Carbonyl Tetrakis(pentafluorophenyl)octachloroporphyrin Ru(II)   Page 12

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12  122   21  37        7  139  224  38        13  479  408  15
13  365  377  19        8   85  115  52        14  247  245  20
14  424  436  19        9  494  478  20        15  360  325  18
15  209  111  27       10  210  140  30        16  950  951  17
16  140   79  35                               17  127   67  35
17  -88   64  46            1  17  1           18  816  764  17
18  114   99  42                               19  649  596  18
19  120   89  42        0  282  217  17         20  109   31  44
20  305  377  24        1  179  190  32         21 -152   49  30
                        2   52    5  67         22  494  464  17
    1  13  1            3  -45   28  71         23  578  546  17
                        4  153   82  35         24  194   75  29
0  745  789  13                                 25  635  609  18
1  179  126  31            2  0  1              26   32   24  80
2  440  399  20                                 27  105   71  48
3  159   38  34        0  340  114  10         28  184   41  34
4  231  237  27        2  719  644  12
5  223  234  28        4  802  738  14             2  3  1
6  242  255  23        6 1181 1048  17
7  132   24  34        8 1970 1778  24         0  178  219  13
8   49   26  62       10 3055 3079  34         1 1135 1224  12
9  164    7  31       12 1455 1368  22         2 2251 2131  15
10 567  577  17       14   97  134  49         3  605  369  11
11 302  328  22       16  247  219  30         4  999 1129  12
12 718  713  17       18  843  887  24         5 1536 1701  16
13 281  261  23       20  991  905  25         6 1977 2090  19
14 405  374  19       22  625  656  27         7 1559 1649  16
15 -136  51  32       24  904  908  24         8  -65   61  37
16 326  295  22       26  185  134  44         9 1306 1282  15
17  -47  97  68       28  549  461  28        10 1219 1251  15
18 499  482  19                               11  122   80  28
                        2  1  1               12 1108 1093  16
    1  14  1                                   13  956  964  15
                      0  240  407   9         14  413  380  17
0  151  107  23        1  683  400   9         15  201  268  24
1  299  262  21        2 1197 1321  12         16 1174 1125  18
2  567  595  17        3 1509 1489  14         17  308  337  21
3  108  119  40        4  812  877  11         18  302  277  22
4  388  420  19        5  186  134  18         19  887  859  18
5   78   55  50        6  365  249  12         20   65    3  60
6  163  176  31        7 1158  984  14         21  472  496  20
7  254  256  23        8 1307 1278  15         22 -148   88  29
8  516  498  18        9 1207 1286  15         23  467  466  18
9  214  100  27       10  418  368  14         24  455  419  19
10 346  334  21       11  435  434  14         25  484  461  19
11 102    0  44       12  694  676  14         26  109  103  46
12 -56   97  61       13  209  198  21         27  615  571  19
13 253  185  25       14  937  864  16
14 472  492  19       15  716  705  16            2  4  1
15  66  134  60       16  477  486  17
16 290  311  25       17  139  157  32         0  281  348  10
                      18  177    4  29         1 2257 2131  21
    1  15  1          19  616  579  18         2 1666 1726  17
                      20  775  752  18         3  192  230  18
0  433  423  13       21  148   29  37         4  337  162  13
1  197   91  27       22  738  688  19         5  612  645  12
2  -74   70  50       23  325  264  21         6  315  467  14
3   69   67  54       24  637  541  18         7 2343 2347  22
4  370  325  20       25  586  537  18         8  291  270  15
5  148  131  34       26  518  467  19         9  153  228  23
6  488  449  18       27  426  364  21        10 1286 1208  16
7  -91   48  44       28  454  494  21        11 1405 1375  17
8  134   25  37                               12  170   73  24
9  133  204  38          2  2  1              13 1027 1056  16
10 229  220  27                               14  669  702  16
11 507  541  19       0  955  948   9         15  189  212  25
12 452  460  20       1  211   73  14         16  148  148  31
13 301  324  24       2 1084  614  12         17 1657 1659  20
                      3 1906 2030  18         18  285  252  23
    1  16  1          4  109  206  27         19  549  546  19
                      5  197  109  17         20  156  222  36
0  150   71  25       6 1379 1372  15         21  496  530  20
1  240  310  25       7  785  866  12         22   73  174  53
2  169   78  32       8  985  833  13         23  691  607  17
3  428  449  19       9 1305 1348  15         24  482  452  19
4  225  141  27      10  929  885  14         25  121  118  42
5  102   21  45      11 1735 1612  19         26  -18  129  92
6  145  100  36      12  658  589  14         27 -116    2  42
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    2  5  1              14 1190 1262  18         6  488  444  17
                        15  169   96  30         7  505  592  17
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1  398  373  12          17  189  230  30         9   30   41  73
2  505  569  12          18  184  215  32        10  116   94  39
3  559  484  12          19  134  204  35        11  571  632  18
4  751  684  12          20  718  745  17        12  699  647  18
5 1786 1556  18          21  264  216  24        13  329  402  22
6  -40   95  50          22  142  224  36        14 -169  227  33
7  540  426  13          23  209  205  29        15  227  193  24
8  782  642  14          24 -150  129  31        16  501  456  17
9  502  482  14          25  -83    9  53        17  505  579  17
10 240  255  19                                  18  354  372  20
11 410  430  15              2  8  1             19  204  181  28
12 335  330  17                                  20   86   59  50
13 1059 1092  16        0  797  819  11          21  -53   62  65
14 626  611  16         1  511  462  14          22 -154   30  31
15 -89   60  39         2  280  284  17          23  543  513  20
16 337  277  20         3  742  752  14
17 1043 1018  18        4  653  698  14              2  11  1
18 262  286  25         5  126  171  29
19 479  478  20         6  891  862  15          0  366  318  13
20 305  300  24         7  337  283  17          1  304  342  20
21 -98  111  41         8  142  110  29          2   87   42  44
22 717  739  17         9  470  484  16          3  746  744  17
23 469  479  19        10  570  573  16          4  172  195  28
24 -90   96  47        11  113   29  35          5  254  216  23
25 117  213  43        12  835  856  17          6  259  185  23
26   3  130 106        13  114   41  38          7  449  507  19
27  14   71  98        14  -67   85  51          8  197   53  28
                       15  218  213  26          9  996 1008  18
    2  6  1            16 -107    0  39          10 145  120  36
                       17 -161  189  27          11 -93   77  45
0  579  541   9        18  473  506  17          12 160   94  35
1  590  552  13        19   41    0  68          13 336  384  19
2 1050 1103  14        20  174  168  31          14 756  724  16
3  233   26  17        21  207  191  28          15 928  930  17
4  283  252  16        22   26  148  82          16 299  251  21
5  140   51  24        23  102  142  47          17 107   84  42
6 1047 1025  15        24  184  195  33          18 267  248  24
7  851  950  14        25  187  134  33          19 496  488  19
8  799  874  14                                  20 237  212  27
9  699  720  14            2  9  1               21 580  551  19
10 647  638  15
11 236  321  20        0  568  599  11              2  12  1
12 178  216  25        1  457  476  15
13 628  596  16        2  566  503  15          0  423  451  14
14 261  234  21        3   38  109  58          1  492  489  18
15 370  385  19        4  113   10  33          2  144  102  34
16 1409 1377  19       5  145  102  28          3  214  128  26
17 257  252  24        6  558  582  16          4  576  628  18
18 653  681  18        7  767  769  16          5  414  319  20
19  54   74  66        8 1023 1096  17          6  370  389  21
20 -67   93  53        9  443  451  17          7  534  502  19
21 270  273  23       10  220  268  24          8  440  427  20
22 738  728  17       11  570  588  17          9  192   55  31
23 111  120  43       12  217  247  25          10 249  106  23
24 -17  169  90       13  651  618  18          11 573  608  17
25 -161  33  30       14  340  337  21          12 290  242  22
26 114  165  47       15  425  477  20          13 494  516  18
                      17  154  184  31          14 154  171  33
    2  7  1            18  241  271  24          15  27   86  78
                      19  757  776  17          16 524  518  18
0   91   40  24       20  460  482  19          17 452  399  19
1  364  359  14       21 -109  121  40          18 374  361  21
2  800  735  14       22 -167   98  27          19 181  232  32
3  251  252  17       23   23   79  87          20 219  217  29
4  807  901  14       24  165  154  36
5  406  275  15                                      2  13  1
6  353  404  16           2  10  1
7  117   81  30                                  0  516  548  14
8 1583 1529  18       0  288  208  14          1  185   23  30
9  195   67  23       1  547  554  16          2  652  586  18
10 419  409  16       2  131  166  31          3  521  510  19
11 169  212  25       3  355  274  18          4  443  398  20
12 177  204  26       4  409  412  17          5  133  106  39
13 194  158  25       5  982  958  17          6  128    0  35
                                               7  183  169  28
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Aquo. Carbonyl Tetrakis(pentafluorophenyl)octachloroporphyrin Ru(II)   Page 13

h	Fo	Fc	σ
8	668	649	16
9	223	274	25
10	345	424	20
11	287	229	22
12	171	121	31
13	335	261	21
14	381	447	20
15	109	133	43
16	252	307	25
17	219	209	28
18	381	383	21

2 14 1

h	Fo	Fc	σ
0	660	638	12
1	185	42	28
2	69	9	52
3	59	97	57
4	124	82	37
5	146	1	33
6	510	474	17
7	212	182	26
8	110	111	41
9	44	27	67
10	354	393	20
11	343	221	21
12	598	669	18
13	155	119	35
14	221	203	28
15	258	203	26
16	309	324	24

2 15 1

h	Fo	Fc	σ
0	87	12	35
1	134	157	36
2	306	322	21
3	282	227	22
4	215	151	26
5	327	363	21
6	111	1	41
7	151	145	34
8	389	362	20
9	352	310	21
10	186	191	31
11	114	118	44
12	-58	0	63
13	186	187	33

2 16 1

h	Fo	Fc	σ
0	216	177	19
1	86	109	50
2	99	96	46
3	133	127	38
4	69	0	56
5	395	402	20
6	104	129	46
7	111	16	44
8	-115	34	39
9	64	90	62

2 17 1

h	Fo	Fc	σ
0	82	12	40
1	161	168	35
2	189	159	31

3 0 1

h	Fo	Fc	σ
0	2946	2686	26
2	432	551	15
4	197	65	23
6	3377	3168	35
8	279	233	21
10	693	720	18
12	597	609	20
14	2750	2698	33

h	Fo	Fc	σ
16	352	288	26
18	910	846	24
20	1352	1303	27
22	-176	30	33
24	670	608	24
26	49	132	88
28	217	69	43

3 1 1

h	Fo	Fc	σ
0	1243	1019	11
1	2138	2032	20
2	455	595	11
3	1759	1543	17
4	2557	2245	23
5	1955	1985	19
6	349	276	13
7	707	693	12
8	-91	135	29
9	-99	28	28
10	272	270	16
11	235	257	19
12	1621	1595	18
13	74	136	42
14	329	321	18
15	189	159	25
16	914	921	17
17	284	256	21
18	635	610	18
19	351	350	21
20	181	114	32
21	427	375	21
22	434	411	18
23	-120	24	36
24	126	1	40
25	126	191	40
26	354	377	22
27	-119	7	41
28	516	519	20

3 2 1

h	Fo	Fc	σ
0	941	768	9
1	1174	1176	13
2	258	417	14
3	702	551	11
4	927	805	12
5	1035	943	13
6	593	621	12
7	542	582	12
8	859	924	13
9	839	917	13
10	928	897	14
11	394	344	15
12	-150	21	20
13	949	912	15
14	615	615	16
15	771	785	16
16	59	22	53
17	210	200	25
18	208	199	27
19	863	882	18
20	125	101	41
21	628	582	19
22	92	2	46
23	483	466	18
24	-104	110	42
25	209	289	29
26	327	319	23
27	65	92	63

3 3 1

h	Fo	Fc	σ
0	1075	1102	10
1	1855	2024	18
2	1490	1347	10
3	323	343	13
4	2022	1938	19

h	Fo	Fc	σ
5	888	806	13
6	-51	165	44
7	628	565	13
8	-53	10	44
9	1010	1002	14
10	150	64	24
11	1584	1540	18
12	125	49	29
13	202	264	23
14	117	86	34
15	461	493	17
16	208	125	25
17	1538	1524	20
18	68	5	55
19	-112	58	39
20	295	342	24
21	507	544	20
22	568	527	17
23	630	615	17
24	-53	73	64
25	-58	132	62
26	179	161	33
27	360	382	23

3 4 1

h	Fo	Fc	σ
0	516	460	9
1	736	840	12
2	412	396	12
3	901	1031	17
4	-99	143	26
5	153	107	22
6	390	405	14
7	1032	996	14
8	228	96	18
9	2071	1968	18
10	157	9	24
11	512	513	15
12	715	719	15
13	925	963	16
14	1024	1006	16
15	461	448	17
16	-37	39	66
17	136	11	35
18	-63	111	56
19	261	290	25
20	154	242	36
21	246	285	24
22	107	162	43
23	208	220	28
24	-86	103	48
25	600	581	19
26	127	123	42
27	471	475	21

3 5 1

h	Fo	Fc	σ
0	242	78	12
1	590	589	12
2	1290	1400	15
3	340	229	14
4	942	917	13
5	186	243	20
6	173	160	21
7	986	939	14
8	531	527	14
9	597	575	14
10	972	964	15
11	1691	1674	19
12	557	567	15
13	449	459	16
14	541	565	16
15	505	513	17
16	1002	972	18
17	759	764	18
18	280	327	24
19	105	126	46
20	357	432	23

h	Fo	Fc	σ
21	8	161	94
22	745	780	17
23	601	551	18
24	-24	17	84
25	483	515	20
26	351	360	23

3 6 1

h	Fo	Fc	σ
0	329	299	10
1	1369	1243	16
2	799	674	13
3	90	71	32
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8	1037	1028	15
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10	202	216	22
11	103	76	36
12	-95	27	35
13	476	430	17
14	960	932	17
15	50	5	60
16	213	208	26
17	-52	118	62
18	-161	15	27
19	121	54	42
20	682	683	17
21	235	155	25
22	179	92	31
23	361	331	21
24	435	418	20
25	184	119	33
26	514	481	20

3 7 1

h	Fo	Fc	σ
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4	1293	1351	16
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6	573	537	15
7	702	771	15
8	98	89	36
9	774	790	15
10	785	790	16
11	639	564	16
12	195	162	25
13	39	134	64
14	-63	174	52
15	379	412	20
16	737	717	18
17	-86	1	47
18	590	628	19
19	238	277	24
20	337	321	21
21	601	610	18
22	668	673	18
23	364	301	21
24	777	743	18
25	363	372	23

3 8 1

h	Fo	Fc	σ
0	1111	1138	12
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2	1412	1352	12
3	120	75	30
4	847	820	15
5	343	306	17
6	278	156	19
7	930	939	16
8	701	686	16
9	-15	91	78

h	Fo	Fc	σ
10	347	361	18
11	-49	94	57
12	441	424	18
13	787	783	17
14	851	815	18
15	58	194	60
16	-106	156	40
17	190	213	31
18	-108	152	37
19	302	304	21
20	761	749	17
21	199	204	29
22	462	471	19
23	269	247	25
24	167	65	35

3 9 1

h	Fo	Fc	σ
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3	214	163	22
4	479	509	16
5	1162	1082	17
6	824	807	16
7	169	213	27
8	418	466	18
9	-92	105	39
10	100	160	41
11	752	714	17
12	737	730	17
13	199	205	28
14	171	148	32
15	70	50	56
16	432	430	17
17	423	443	18
18	262	265	23
19	221	261	26
20	180	215	30
21	-70	70	55
22	-86	2	49
23	656	653	19

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h	Fo	Fc	σ
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1	889	885	16
2	465	413	17
3	806	809	16
4	55	2	54
5	-82	41	42
6	183	177	27
7	776	761	17
8	111	4	39
9	487	496	18
10	384	449	20
11	167	167	32
12	253	174	25
13	390	387	21
14	131	157	40
15	678	658	16
16	282	250	22
17	-20	31	82
18	191	231	28
19	226	213	26
20	137	102	37
21	635	663	18
22	141	198	39

3 11 1

h	Fo	Fc	σ
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1	656	682	17
2	180	168	28
3	390	350	19
4	469	530	18
5	660	599	17
6	182	139	29

h	Fo	Fc	σ
7	635	654	18
8	106	82	43
9	57	63	61
10	485	448	19
11	859	823	19
12	131	151	35
13	523	535	17
14	328	250	20
15	107	239	41
16	174	157	30
17	295	278	22
18	-157	1	27
19	294	302	23
20	-98	49	45
21	144	6	38

3 12 1

h	Fo	Fc	σ
0	78	74	38
1	-140	37	29
2	322	274	21
3	790	787	18
4	250	125	25
5	471	418	19
6	40	22	71
7	72	15	55
8	355	255	22
9	749	752	16
10	154	137	31
11	-15	220	86
12	162	124	31
13	248	304	24
14	349	304	20
15	285	315	23
16	-129	35	34
17	157	173	34
18	277	283	24
19	-124	57	37

3 13 1

h	Fo	Fc	σ
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1	335	377	22
2	308	252	23
3	195	94	26
4	148	91	31
5	499	467	17
6	847	884	16
7	304	137	21
8	306	397	21
9	88	40	47
10	191	133	28
11	153	112	33
12	395	367	20
13	124	56	39
14	-105	79	41
15	218	270	28
16	309	286	23
17	40	65	74

3 14 1

h	Fo	Fc	σ
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5	-71	9	51
6	102	141	43
7	180	198	29
8	599	584	17
9	181	184	30
10	142	272	36
11	169	110	32
12	-15	1	91
13	131	27	39
14	322	318	23
15	-88	81	50

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```
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 0  214  216 19
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 2  122  121 38
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12  139  194 39

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 9  338  306 23

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26  203  168 42

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 8 1934 1987 19
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10  724  703 14
11 1178 1240 16
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13   65   73 47
14  946  957 16
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24  285  231 24
25   66   72 60
26  541  503 19
27  148   68 39


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17   23  132 79
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19  173  210 32
20  194  207 31
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22  183  190 30
23  -77  182 51
24  408  423 20
25  516  480 19
26   98    3 50
27  239  231 29

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26  127   57 42
27  460  451 21

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 3 1856 1812 13
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 5 1356 1452 16
 6 2087 2063 21
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12  321  361 18
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Aquo. Carbonyl Tetrakis(pentafluorophenyl)octachloroporphyrin Ru(II) Page 15

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 3  632  630  13       21  325  379  21    13  160  143  33   13  333  343  20     9  210  218  29     17  349  400  21
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 7  107   93  30       25  187  236  33    17  -62   27  55   17  259  278  25                         21  537  543  18
 8  357  252  15                           18 -129   25  33   18  102    1  47     0  150  149  27     22  121  189  40
 9 1249 1181  16           5   6  1        19 -173   17  24   19 -139   30  34     1  309  260  23     23  186  151  31
10  967  983  15                           20  195  251  29                        2  141  110  38     24  103   36  47
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Aquo. Carbonyl Tetrakis(pentafluorophenyl)octachloroporphyrin Ru(II)

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Aquo. Carbonyl Tetrakis(pentafluorophenyl)octachloroporphyrin Ru(II)

```
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 3  415  374 17      3  867  888 18     13  339  358 22     16  217  256 27     11  305  318 21      9  131   89 37
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Aquo. Carbonyl Tetrakis(pentafluorophenyl)octachloroporphyrin Ru(II)

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12  363  343  20      10  273  273  31      14  434  431  20      15  239  236  24       0  116  177  29      18  182  215  41
13  394  458  20      12  124   37  51      15  595  645  16      16  580  560  18       1 -125   47  34      20  363  406  29
14 -166   24  26      14  316   21  32      16  582  560  17      17   94    4  47       2  288  199  22
15  299  324  23      16  858  828  22      17  202   20  27      18  321  337  22       3  540  509  17        10   1  1
16  174  191  33      18 -104   82  52      18  420  418  19      19  581  587  19       4  339  297  20
17  312  270  24      20   56  118  72      19  338  320  21      20  191  209  31       5  711  741  17       0  748  720  12
                      22  491  493  27      20  194  255  29      21  154  201  49       6  141   54  35       1  150  110  32
     8  11  1                               21  244  268  26                             7  252  259  24       2  581  532  17
                          9   1  1          22  186  219  32          9   7  1           8  113   80  41       3   96  148  43
 0  538  529  12                                                                         9   95  142  46       4  591  608  17
 1  480  461  18       0  -45  142  44          9   4  1           0  379  401  14      10  216  212  27       5   64  156  54
 2  405  385  19       1  216  183  23                             1  183   63  30      11  215  263  28       6  262  245  23
 3  155   94  32       2 2009 1991  22       0  245  145  16       2 1250 1242  19      12 -156   23  29       7  699  737  17
 4  245  135  24       3  354  377  18       1 1693 1674  20       3  496  469  19      13  163  184  34       8  346  315  20
 5  941  952  17       4  216  215  23       2  316  298  20       4  466  453  19      14  -92   93  48       9  306  286  22
 6  374  277  19       5  385  382  18       3  -63   43  50       5  519  494  19      15  218  207  29      10  237  271  25
 7  690  715  17       6  182  252  26       4  391  387  18       6  304  309  23      16  -77  120  55      11  581  570  18
 8  321  277  21       7 1011  969  17       5 1232 1228  18       7  167  148  32                           12  163   90  33
 9  159  112  32       8 1333 1408  18       6  261  296  22       8  771  837  18          9  11  1         13  308  274  20
10  215   96  27       9  643  641  17       7   82   65  47       9  100   39  46                           14  373  298  19
11  812  801  17      10  371  382  19       8  -79  100  45      10  565  604  16       0   93  138  35      15  457  465  18
12  111   64  42      11  147  162  33       9  804  788  17      11  122   63  36       1  512  485  18      16  598  611  17
13  271  287  24      12  239  109  25      10  961  925  18      12   83   88  47       2  427  374  19      17  420  397  19
14 -130   21  35      13 1426 1427  20      11 1399 1373  20      13  297  287  21       3  731  773  17      18  499  488  18
15  169  141  34      14 1106 1133  19      12  157   51  33      14  284  256  22       4  209  116  27      19 -101  106  42
16  418  456  21      15  300  234  20      13  664  677  19      15  191  216  29       5  141  137  36      20  232  226  27
                      16  224   34  24      14  103   71  40      16   92  100  48       6  335  333  21      21  370  367  21
     8  12  1         17   87   24  47      15  516  496  17      17  206  211  29       7  361  363  20
                      18  301  326  21      16  579  573  17      18  474  541  20       8  304  222  22          10   2  1
 0   35   70  58      19 -147   45  28      17  488  534  18      19  137  135  39       9  478  461  19
 1  317  346  21      20  -58  156  53      18  -74   39  51      20  497  492  20      10  197  200  29       0  664  622  12
 2  496  428  18      21 -169   28  25      19  289  330  23                            11  108   81  44       1 1398 1342  19
 3  582  634  17      22  286  320  24      20  161  190  34          9   8  1          12   96   51  49       2  -67   26  51
 4  634  550  17      23  386  368  21      21  110  124  45                            13  358  330  22       3  913  900  17
 5  469  499  18                            22  444  464  21       0  572  571  14      14  125   47  43       4  -97   12  39
 6  189  118  29          9   2  1                                 1  542  492  19                            5  488  460  18
 7  196  124  28                                9   5  1           2  224  165  27          9  12  1          6  489  455  18
 8  247  227  24       0  837  845  12                             3  408  430  20                            7 1181 1211  18
 9  284  288  23       1  634  602  16       0 -135   50  21       4  600  590  19       0  475  372  14       8  421  438  19
10  296  312  23       2 1075 1051  17       1  450  433  18       5  477  439  20       1  428  414  20       9  284  296  23
11  132  134  39       3  445  447  17       2  112   39  38       6  356  324  22       2  154   80  34      10  415  432  20
12  187  106  31       4  646  623  16       3 1197 1186  18       7  387  378  21       3  216  222  27      11  655  642  18
13   20  136  89       5  550  568  16       4  519  467  18       8  453  471  17       4  292  253  23      12  409  392  21
14  314  303  24       6  738  777  16       5  313  348  21       9  324  335  20       5  550  540  18      13  663  646  16
                       7  142   32  31       6  284  258  22      10   33  153  72       6  199  214  29      14  389  405  18
     8  13  1          8  290  342  21       7  470  436  18      11  540  541  17       7  132   39  38      15  729  720  17
                       9   56   25  57       8  486  496  18      12  -80   84  47       8 -109  115  40      16  131  178  36
 0  610  652  13      10  798  789  17       9  779  784  18      13  231  260  25       9   95   42  48      17  514  545  18
 1  121   25  40      11 1097 1068  18      10  213   92  27      14  346  361  21      10 -107   59  42      18  247  252  25
 2  153  148  34      12 1219 1205  19      11  580  535  18      15  158  201  34      11  374  420  22      19  255  273  25
 3  203   57  28      13  397  254  20      12  147  190  36      16  280  365  24                            20  413  448  20
 4  393  407  20      14  235   71  27      13   85   22  45      17  241  244  27          9  13  1          21  255  212  26
 5  183  234  30      15  475  481  17      14  931  901  16      18  483  493  20
 6  529  511  18      16  756  779  16      15  847  876  16      19  265  259  26       0  124  177  30          10   3  1
 7  235  189  26      17  905  908  17      16  514  509  17                             1  205  137  30
 8  184  170  31      18  257  305  23      17  179  232  30          9   9  1           2  428  427  20       0  153  162  23
 9  -83   18  50      19 -108   15  38      18  242  270  25                             3  236  258  27       1  254  234  23
10  342  317  22      20  -87   35  46      19  365  341  21       0  159  116  26       4  -48   21  68       2  153  178  32
11  199  254  31      21 -118   37  37      20  552  578  19       1  446  484  21       5   97  131  47       3  282  311  22
                      22 -102   62  43      21  511  508  20       2  395  315  20       6  140  132  38       4  173   30  30
     8  14  1         23  473  475  20                             3  749  704  16       7  -93   11  47       5 1371 1352  19
                                                9   6  1           4  230  123  24       8  250  274  26       6  668  628  18
 0  -94   53  34          9   3  1                                 5  -39   49  68                            7  454  378  19
 1 -121    0  37                             0  937  910  13       6  133   96  35          9  14  1          8   82   98  49
 2  569  599  18       0  162  194  20       1   87   15  46       7  642  641  17                            9  129  116  38
 3  120   12  41       1   89  181  41       2  423  429  19       8  384  410  19       0  344  360  23      10  465  439  19
 4   70  161  57       2  102  163  38       3  197   22  27       9  642  596  17                            11  539  575  19
 5 -137   81  33       3  299  286  20       4 1264 1244  19      10  -88   69  43          10   0  1         12  116  152  37
 6  135   20  39       4  151   97  30       5  508  487  18      11   73   54  53                            13  216  237  25
 7   92   53  50       5  -72   42  46       6  464  405  19      12  -50   64  63       0 1345 1307  19      14  116  144  38
                       6  470  504  17       7  139    2  35      13 -145   15  30       2 1776 1653  27      15  331  331  20
     9   0  1          7  671  658  17       8  383  398  20      14  242  254  26       4 -111   75  47      16  157  197  32
                       8  346  322  20       9  324  282  22      15  107  163  45       6  884  944  24      17  686  686  17
 0  751  752  16       9  611  594  17      10 1251 1225  19      16  236  263  27       8 1652 1656  27      18 -134   80  32
 2  646  683  22      10  379  376  20      11  647  646  19      17  247  153  27      10  678  714  25      19  269  271  24
 4 1423 1478  24      11  348  320  21      12  409  437  18                            12  271  260  34      20  128  101  40
 6  265  322  29      12  508  468  19      13  725  719  16          9  10  1          14 1248 1258  23      21  406  383  21
 8  246  123  31      13  984  947  18      14  270  217  22                            16  200  120  38
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Aquo. Carbonyl Tetrakis(pentafluorophenyl)octachloroporphyrin Ru(II)

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10   4  1        5   842  787  19     3   158  164  34    10   355  378  19    11   6  1          0    21    8  69
                 6   636  601  16     4   112   43  43    11   666  725  16                       1   -65   86  57
0   156  195  23  7   205  149  26     5   714  703  18    12   430  428  18    0   713  678  12   2    87  135  50
1   135  118  35  8   600  578  17     6   234   52  27    13   219  269  25    1   359  381  19   3   326  337  22
2  1271 1231  19  9   479  410  17     7   304  302  23    14   231  231  25    2   523  499  17   4   405  416  20
3    88   73  47 10   397  403  19     8   240  229  27    15   -88   13  45    3   428  428  18   5   337  282  22
4   166  198  31 11   -77   89  48     9   123  116  41    16   240  211  25    4   558  550  17   6   491  489  19
5   250  191  24 12   580  536  17    10   233  232  27    17   607  646  18    5   135   94  35   7   142   15  37
6   -87  101  45 13   303  291  22    11   248  248  27    18  -163   18  28    6   556  566  17   8   377  347  21
7   121  134  39 14    67  106  55                         19   125  191  41    7    63    8  56   9   441  476  20
8   463  487  19 15  -120   35  35    10  12  1                                 8   649  668  17  10   410  412  21
9   479  541  19 16   402  352  20                         11   3  1            9    83  117  48  11   -61   38  61
10  339  380  22 17  -143   97  32    0   265  303  18                         10   499  475  18
11  330  335  19 18   555  553  19    1    85  115  53    0   112  108  31     11    99   58  43   11  11  1
12 -114   90  34                      2   302  281  24    1   333  363  22     12   412  410  19
13  269  236  22   10   8  1          3   148  166  37    2   115  117  42     13    73  118  53   0  -136  138  25
14  414  406  18                      4    39   77  75    3   217  176  28     14   335  361  21   1   354  371  22
15  391  421  19  0   496  501  12    5   140   94  39    4   574  521  19     15    30  150  79   2    95   87  50
16   38  124  70  1   -37   40  69    6   172  209  34    5   599  617  19     16   278  273  24   3   211  203  29
17  -50   53  63  2   123  128  37    7   228  265  28    6   558  592  19     17   142  167  38   4   305  291  24
18   24   94  82  3   223  261  25    8   402  374  21    7    56   20  63                         5   185   55  32
19  628  642  18  4  -132   41  31                        8    94   90  48     11   7  1          6   319  312  23
20  398  348  21  5   116   89  39    10  13  1           9   458  451  17                         7   627  571  19
                  6   605  635  17                       10   369  411  19     0   866  886  12   8   166  128  35
10   5  1        7   537  428  17    0   126  131  32    11   340  370  20     1   587  568  17
                  8  1128 1108  17    1   -71   89  59    12   -91    1  42     2   736  740  17   11  12  1
0   856  842  13  9   236  191  24    2    63   23  64    13   610  626  17     3    -7   25  94
1    62   77  58 10   105   86  42    3    52    3  86    14  -131   62  32     4   103  168  43   0  -107   49  33
2    67    4  56 11   -45   93  65                        15   495  528  18     5   351  325  20   1  -105   33  45
3   624  625  18 12   428  349  19    11   0  1           16   462  510  19     6  1043 1045  17   2    55  131  68
4   545  539  19 13   142  193  35                        17   233  281  26     7   217  245  26
5   177  139  31 14   271  354  24    0   453  434  19    18   114  175  43     8   -90   14  44   12   0  1
6   829  841  18 15   250  257  26    2   773  823  25    19   306  317  24     9    84  111  48
7   577  568  19 16   309  335  23    4  -156   25  38                         10   -59   93  57   0   407  458  21
8   179  115  31 17   242  250  28    6   311  353  31    11   4  1           11   151    8  33   2   -71  140  73
9   545  560  19                      8   429  468  28                        12   846  859  17   4   300  281  29
10  260  256  22   10   9  1         10   285  376  29    0   148  181  26    13    89   68  49   6  1767 1846  26
11  537  546  17                     12   777  815  23    1   284  295  24    14   227  273  27   8   868  801  23
12  -73   59  49  0   104  148  32   14  -146   47  39    2   454  458  20    15   241  253  26  10   159   70  43
13  146  204  33  1   108   50  42   16   673  713  24    3   762  774  18    16   254  236  26  12   439  472  26
14  202  228  27  2  -184    8  22   18   634  704  25    4   265  252  25                       14   193  202  40
15  469  449  18  3   189  200  29   20   154  171  50    5   522  485  19    11   8  1         16    92  164  65
16  104  149  43  4  -124   25  34                        6   156  210  35
17   85  139  49  5   285  277  22   11   1  1            7    35   59  69    0   615  586  12   12   1  1
18  151  215  35  6   349  307  20                        8   265  316  22    1   205  143  27
19  404  395  21  7   156   15  33   0   617  573  13     9   565  580  17    2   577  571  17   0   136  226  29
20  237  190  28  8   197  165  28   1   479  498  19    10    97   31  43    3   242  210  24   1  -122   99  38
                  9   586  600  17   2   584  558  18    11   983 1001  17    4   647  684  17   2  -174   88  26
10   6  1       10   370  336  20   3   791  761  18    12    67  167  54    5   486  419  18   3  -147  140  27
                 11   324  276  21   4   -50   43  64    13    87   93  47    6   147   71  34   4   385  469  18
0   434  408  14 12   144  110  35   5   -54   96  61    14    38   83  70    7    37  103  72   5    54  111  59
1   342  333  22 13   432  428  20   6   534  506  19    15   389  397  20    8   108   54  42   6   262    2  22
2   404  357  20 14   284  298  24   7  -139   18  31    16   154  128  34    9   112  118  41   7   372  291  19
3   134  115  38 15   173   59  34   8   521  563  19    17  -169  105  26   10   226  173  26   8   753  774  16
4    80   64  52                     9   263  193  25    18  -170   12  27   11   176  164  31   9   407  415  18
5   231  211  27   10  10  1        10   150  203  31                        12   142  110  36  10   821  858  17
6   159  162  34                    11   -50   16  60    11   5  1          13   174  185  32  11   -56  163  58
7   157  163  35  0   227  216  19  12   512  502  17                       14    86  134  52  12   132  166  36
8   377  315  18  1   376  349  20  13  -158   17  26   0   256  249  18    15   -57   60  63  13  -125   73  34
9   522  494  17  2   259  157  24  14   297  288  21   1   481  491  20                       14    85  161  49
10 -116    9  34  3   548  560  18  15   453  476  18   2   318  308  23    11   9  1         15  -104   62  41
11   81   78  48  4   -78    7  50  16   193  134  29   3   -49   26  67                       16   359  377  21
12  206  213  26  5  -164   69  26  17   247  228  25   4   -51   62  66    0   283  259  16  17  -166   71  28
13  484  489  18  6   283  233  23  18   213  240  28   5   526  488  17    1   562  545  18
14  456  463  18  7   908  882  17  19   165  246  34   6   203  252  26    2   433  427  19   12   2  1
15  111  116  41  8   260  209  24                      7  -119   63  34    3   717  711  17
16 -110   33  38  9   198  117  29   11   2  1          8   114  199  39    4   138   13  36   0   628  626  14
17  -72   15  54 10  -120   18  36                      9   393  404  19    5   428  365  19   1   226  312  24
18  522  502  19 11   76   80  54   0   529  494  13   10   306  323  21    6   386  386  20   2   190  262  27
19  140    4  39 12  238  182  27   1   -60  134  59   11   308  333  21    7   518  505  18   3  -168   42  24
                 13  423  416  21   2   606  617  18   12   -68   90  52    8   200  140  29   4   819  792  16
10   7  1       14  -67  111  60   3   221  240  27   13   358  400  20    9   324  272  22   5   561  578  17
                                    4   587  631  18   14   215  241  27   10   403  482  20   6   248  191  23
0   260  278  18   10  11  1        5   146  269  35   15   362  386  21   11   278  279  24   7  1087 1094  17
1  -115  100  39                    6   557  579  19   16    73   76  55   12   265  280  25   8   254  125  23
2   809  789  19  0  -101    0  32   7   189  132  30   17  -132   24  34   13   121  174  43   9   243  180  24
3   -62   11  59  1   310  284  23   8    96  102  47   18   316  331  23                      10   208  137  26
4   -67   57  57  2   308  291  23   9   489  475  17                        11  10  1
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Aquo. Carbonyl Tetrakis(pentafluorophenyl)octachloroporphyrin Ru(II)

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11   135   160   35        1   124     2   38                                    1   621   603   17         0   152   211   27        9   204   142   30
12   -68    74   53        2   878   903   17      13    0    1                   2   195    19   29         1   499   481   20        10  363   321   22
13   232   243   25        3   119   128   39                                     3   743   667   17         2   137   141   40
14   243   321   25        4  -119    36   36      0   200    97   28             4   -86    81   47         3   266   225   26           14    5    1
15  -168    36   26        5   383   407   20      2    68   108   72             5   252   239   24
16   182   277   31        6   313   308   22      4   612   690   24             6   525   487   18           14    0    1             0   308   273   17
17  -149   101   31        7   -76    50   50      6   563   543   24             7    91    89   48                                     1   183   158   32
                           8  -135    93   32      8   741   732   24             8   293   306   23          0   650   609   18         2   246   166   27
   12    3    1            9   -72   120   52      10  765   720   24             9   784   778   18          2   292   287   32         3   666   679   18
                           10  -75    76   51      12  239   194   36             10  262   223   24          4   588   410   25         4   367   316   22
0    368   392   14        11  129   112   38      14  542   574   26             11  267   243   24          6   539   495   26         5   139     3   39
1    341   344   20        12  520   552   19                                     12  116   171   42          8   552   523   26         6   377   355   21
2    228   234   25        13  -78    84   51      13    1    1                   13  286   304   24          10  400   249   29         7    86   125   53
3    503   558   17        14  332   383   22                                                                12  395   354   30         8   521   455   19
4    235   162   24                               0   994  1003   13                13    5    1
5    401   398   19           12    7    1        1   446   479   18                                           14    1    1               14    6    1
6    827   796   17                               2   114   135   41             0   454   449   13
7    385   397   19        0   318   329   15      3   502   537   18             1   395   392   20          0   259   254   18         0   829   817   13
8    398   402   19        1   256   173   24      4    82   128   50             2   190    43   29          1   254   237   25         1   219    61   29
9    964   989   17        2   686   621   17      5   -22    53   82             3   127   103   39          2   474   487   19         2   541   497   19
10  -134    93   31        3   136    46   36      6   803   840   17             4   196    98   29          3   423   366   20         3   214    73   29
11   421   433   19        4   705   675   17      7    33    50   74             5   109   123   43          4  1173  1142   19         4   500   485   20
12    32   134   74        5    93    49   47      8   708   673   17             6   441   396   19          5   311   284   23         5   386   410   22
13    81   110   50        6   395   402   20      9   222   193   26             7   411   417   20          6   227   129   27         6   579   576   19
14   114    19   42        7   181   215   30      10  191   108   29             8   190   142   30          7   450   420   19
15   580   608   18        8   113   170   42      11  112   205   42             9   170   176   32          8   511   492   19           14    7    1
16   268   309   25        9   -56    95   61      12  590   555   18             10  162    22   34          9   347   306   22
17   -92   179   48        10  305   278   23      13  552   512   18             11  623   644   18          10  797   811   18         0   290   251   18
                           11  159    81   34      14  452   461   20             12  302   344   24          11  -64   125   60         1   384   290   22
   12    4    1            12  425   449   20      15  242   265   27                                                                   2  1036  1036   19
                           13  108   155   45                                       13    6    1               14    2    1             3   261   102   27
0    171   196   22                                  13    2    1
1    347   407   20           12    8    1                                       0   455   449   14          0   444   446   14           15    0    1
2    402   396   19                               0   874   854   13             1   261   142   24          1   614   565   18
3   1145  1153   17        0   417   451   14      1   465   396   18             2   805   751   18          2   171   104   32         0   242   231   27
4    282   286   22        1   199   144   29      2   337   313   21             3   278   197   24          3   605   560   18         2   489   539   28
5    -23   121   80        2   398   442   20      3    16    72   87             4   437   438   19          4   400   309   20         4   606   592   27
6    104   127   42        3   371   355   20      4    90   123   47             5   201   110   29          5   184   123   31         6   470   515   28
7    -41   103   68        4   273   240   24      5  -137    44   31             6    10    37   95          6   623   594   18
8   -136     7   31        5   166    39   33      6   293   243   22             7   -91   116   47          7   478   415   19           15    1    1
9    123   211   38        6   411   397   20      7   281    80   23             8   499   458   19          8   149   155   36
10   190   242   28        7   206   149   29      8   531   472   18             9   453   429   20          9   220   196   28         0   621   613   14
11   248   312   24        8   215   258   28      9   534   513   18             10  519   503   19          10  384   365   21         1   262   277   26
12   167   152   31        9   112   196   43      10  264   256   24             11  176    95   33          11  152   114   36         2   323   228   23
13   596   635   18        10  -56    34   63      11  382   359   20                                                                   3   629   568   19
14   222   126   27        11  -67     1   58      12  145    70   36                13    7    1               14    3    1             4   650   597   19
15   346   379   22        12  131   108   40      13  304   240   23                                                                   5   355   368   22
16    57   141   65                               14  189   158   31             0   796   798   13          0   244   241   18         6   464   422   20
                              12    9    1        15  380   371   21             1   180    75   32          1   456   389   19
   12    5    1                                                                  2   250   216   26          2   361   345   21           15    2    1
                           0  -148    18   22        13    3    1               3    56    37   64          3   860   825   18
0    638   636   12        1   -71    63   55                                    4  -133    28   34          4   407   418   20         0   379   422   15
1    -74    53   50        2    89    86   50      0   335   295   15             5   138    74   38          5   222   250   28         1   323   287   23
2    431   409   18        3   662   634   18      1   843   804   17             6   680   676   18          6   147   107   36         2   579   572   19
3    316   317   21        4   232   135   27      2   235   214   25             7    89   105   51          7   588   530   19         3   590   581   19
4    448   462   18        5   313   327   23      3   226   155   26             8   305   265   24          8   -37     9   75         4   175   104   34
5    501   507   18        6   191     3   31      4   459   418   19             9   229   184   28          9   561   535   19         5   203     8   31
6   -148    43   29        7   234   145   27      5   304   351   22             10  316   286   23          10  169   141   34
7    289   306   22        8   403   407   21      6   129    35   38                                                                     15    3    1
8    193   260   28        9   104    87   47      7  1034  1036   18                13    8    1               14    4    1
9   -139     2   30        10  139   111   52      8   226   212   26                                                                   0   390   351   15
10   143    54   35                               9   247   272   25             0   280   247   18          0   374   437   15         1   635   648   19
11   241   300   25           12   10    1        10  117   105   41             1   102    57   47          1   906   855   18         2   173    69   35
12  -132    74   33                               11  399   429   20             2   386   367   21          2   175   129   32         3   122   102   44
13    78   140   53        0  -133    55   26      12  180   161   31             3   520   507   19          3    36     4   76         4   183   147   33
14   265   289   25        1   171   267   34      13  667   632   18             4   567   550   19          4   319   242   23
15   358   375   22        2   251   227   26      14  398   366   21             5   203    56   30          5   703   700   18           15    4    1
                           3    86   186   52                                    6   460   441   20          6   241   151   27
   12    6    1            4   207   128   30        13    4    1               7   117    59   44          7   527   515   19         0   280   270   18
                           5   640   665   19                                                                8   316   232   23         1   327   331   24
0    258   259   17        6   213   163   30      0   331   312   15                13    9    1
```

Appendix 5

Transient Spectra of RuTFPPCl$_8$(CO)
at 415 nm
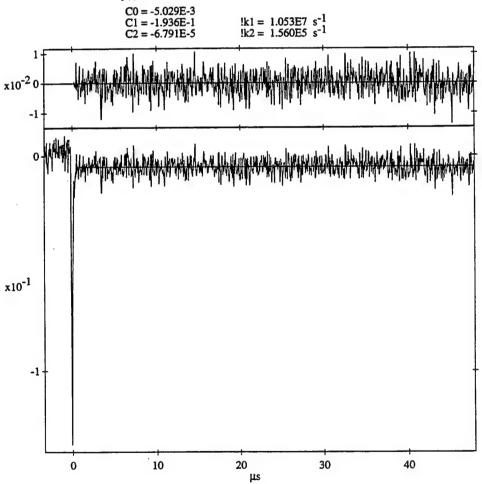
DATA FILE: RUO2.001   1995-2-23 9:19:52
TIME RANGE: 50 µs   INPUT V RANGE: 0.320V   INPUT OFFSET: 0 %
EXPERIMENT: TRANSIENT ABSORBTION
FAST (200 MHz) QUASI-DIFFERENTIAL AMP
                              MODE: SINGLE-ENDED

SHOTS PRE CYCLE: 10   CYCLES: 5   PMT VOLTIGE: 702 V
EXCITATION WAVELENGTH: 355 nm OBSERVATION WAVELENGTH: 415 nm
SAMPLE: RuCl8(CO)
SOLVENT: CH2Cl2
TEMPERATURE: rt
COMMENT: under dioxygen
COMMENT:

---> FIXED PARAMETER;   ! ---> FIXED SIGN

$$y(t) = C0 + C1 * e^{-k1*t} + C2 * e^{-k2*t}$$

$C0 = -5.029E-3$

$C1 = -1.936E-1$ $!k1 = 1.053E7 \ s^{-1}$

$C2 = -6.791E-5$ $!k2 = 1.560E5 \ s^{-1}$

DATA FILE: RUET.002
TIME RANGE: 50 μs   INPUT V RANGE: 0.320V   INPUT OFFSET: 0 %
1995-2-23   9:24:35
EXPERIMENT: TRANSIENT ABSORBTION
FAST (200 MHz) QUASI-DIFFERENTIAL AMP
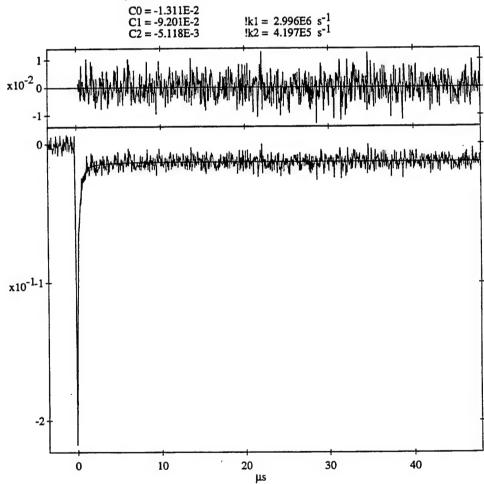   MODE: SINGLE-ENDED

SHOTS PRE CYCLE: 10   CYCLES: 5   PMT VOLTIGE: 702 V
EXCITATION WAVELENGTH: 355 nm OBSERVATION WAVELENGTH: 415 nm
SAMPLE: RuCl8(CO)
SOLVENT: CH2Cl2
TEMPERATURE: rt
COMMENT: under ethylene
COMMENT:

---> FIXED PARAMETER;   ! ---> FIXED SIGN

$$y(t) = C0 + C1*e^{-k1*t} + C2*e^{-k2*t}$$

C0 = -1.311E-2
C1 = -9.201E-2   !k1 = 2.996E6 s^{-1}
C2 = -5.118E-3   !k2 = 4.197E5 s^{-1}

DATA FILE: RUAR.005
TIME RANGE: 50 μs   INPUT V RANGE: 0.320V   INPUT OFFSET: 0 %   1995-2-23 9:14:31
EXPERIMENT: TRANSIENT ABSORBTION
FAST (200 MHz) QUASI-DIFFERENTIAL AMP
                  MODE: SINGLE-ENDED
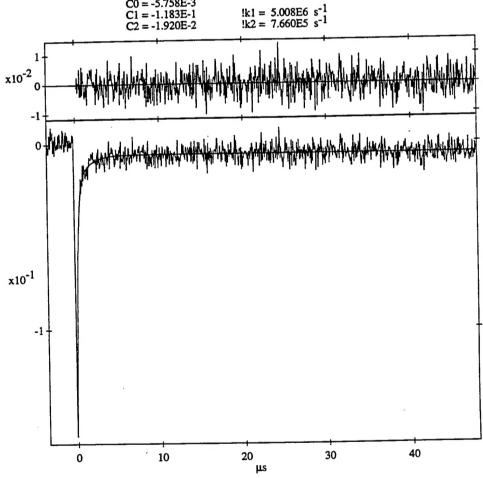
SHOTS PRE CYCLE: 10   CYCLES: 5   PMT VOLTIGE: 702 V
EXCITATION WAVELENGTH: 355 nm OBSERVATION WAVELENGTH: 415 nm
SAMPLE: RuCl8(CO)
SOLVENT: CH2Cl2
TEMPERATURE: rt
COMMENT: under argon
COMMENT:

---> FIXED PARAMETER; ! ---> FIXED SIGN

$$y(t) = C0 + C1 * e^{-k1*t} + C2 * e^{-k2*t}$$

C0 = -5.758E-3
C1 = -1.183E-1   !k1 = 5.008E6 s^{-1}
C2 = -1.920E-2   !k2 = 7.660E5 s^{-1}

DATA FILE: RUO2.000   1995-2-23   9:18:40
TIME RANGE: 5.0 μs   INPUT V RANGE: 0.320V   INPUT OFFSET: 0 %
EXPERIMENT: TRANSIENT ABSORBTION
FAST (200 MHz) QUASI-DIFFERENTIAL AMP
                              MODE: SINGLE-ENDED

SHOTS PRE CYCLE: 10   CYCLES: 5   PMT VOLTIGE: 702 V
EXCITATION WAVELENGTH: 355 nm   OBSERVATION WAVELENGTH: 415 nm
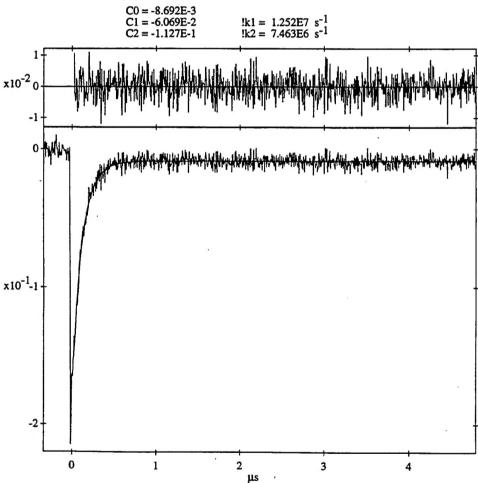SAMPLE: RuCl8(CO)
SOLVENT: CH2Cl2
TEMPERATURE: rt
COMMENT: under dioxygen
COMMENT:

---> FIXED PARAMETER;   ! ---> FIXED SIGN

$$y(t) = C0 + C1*e^{-k1*t} + C2*e^{-k2*t}$$

$C0 = -8.692E-3$

$C1 = -6.069E-2$ $!k1 = 1.252E7 \ s^{-1}$

$C2 = -1.127E-1$ $!k2 = 7.463E6 \ s^{-1}$

DATA FILE: RUET.001   1995-2-23   9:23:24
TIME RANGE: 5.0 μs   INPUT V RANGE: 0.320V   INPUT OFFSET: 0 %
EXPERIMENT: TRANSIENT ABSORBTION
FAST (200 MHz) QUASI-DIFFERENTIAL AMP
                            MODE: SINGLE-ENDED

SHOTS PRE CYCLE: 10   CYCLES: 5   PMT VOLTIGE: 702 V
EXCITATION WAVELENGTH: 355 nm OBSERVATION WAVELENGTH: 415 nm
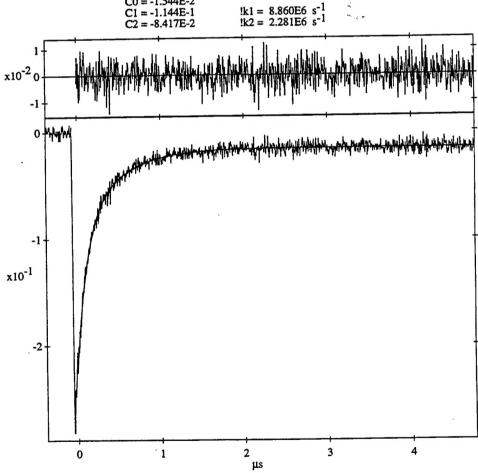SAMPLE: RuCl8(CO)
SOLVENT: CH2Cl2
TEMPERATURE: rt
COMMENT: under ethylene
COMMENT:

---> FIXED PARAMETER;   ! ---> FIXED SIGN

$$y(t) = C0 + C1*e^{-k1*t} + C2*e^{-k2*t}$$

C0 = -1.544E-2
C1 = -1.144E-1   !k1 = 8.860E6 s^{-1}
C2 = -8.417E-2   !k2 = 2.281E6 s^{-1}

DATA FILE: RUAR.004   1995-2-23   9:13:21
TIME RANGE: 5.0 μs   INPUT V RANGE: 0.320V   INPUT OFFSET: 0 %
EXPERIMENT: TRANSIENT ABSORBTION
FAST (200 MHz) QUASI-DIFFERENTIAL AMP
                            MODE: SINGLE-ENDED

SHOTS PRE CYCLE: 10   CYCLES: 5   PMT VOLTIGE: 702 V
EXCITATION WAVELENGTH: 355 nm OBSERVATION WAVELENGTH: 415 nm
SAMPLE: RuCl8(CO)
SOLVENT: CH2Cl2
TEMPERATURE: rt
COMMENT: under argon
COMMENT:

---> FIXED PARAMETER;   ! ---> FIXED SIGN

$$y(t) = C0 + C1*e^{-k1*t} + C2*e^{-k2*t}$$

C0 = -9.262E-3
C1 = -6.495E-2 $!k1 = 7.124E6 \ s^{-1}$
C2 = -8.926E-2 $!k2 = 2.166E6 \ s^{-1}$